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TECHNICAL REPORT No. 3

Low Temperature Fluorination of Aerosol and
Condensed Phase Sol Suspensions of Hydrocarbons
Utilizing Elemental Fluorine

by

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This report outlines the development of a new concept in low temperature direct fluorination. This method involves the reaction of gaseous elemental fluorine upon a solid-phase particulate aerosol at temperatures below room temperature. The rationale for the development of this method is that is a flow process but preserves the low temperature, solid phase fluorination features of the low temperature gradient reactor system developed by Adcock, Marashin and Lagow while eliminating the inherent

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reliance on low temperature mass transport which results in long reaction times and the essentially batch nature of gradient reactor process.

This report discusses the development of a reliable aerosol fluorinator capable of achieving high yields of perfluorinated hydrocarbons via a photochemical fluorination stage. The aerosol system also produces partially fluorinated species in a controlled manner in high yields. Data presented suggests that fluorine reacts preferentially with methyl group hydrogens in the order $CH_3 > CH_2F > CHF_2$. Data also shows that HF produced in the reactor does not solvolyse acid sensitive groups.

S/N 0102- LF- 014- 6601

THE

LOW TEMPERATURE FLUORINATION OF AEROSOL

SUSPENSIONS OF HYDROCARBONS

UTILIZING ELEMENTAL FLUORINE

by

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Abstract

This work describes a new concept in direct fluorination methodology
and an apparatus designed to achieve conditions necessary for the rapid,
continuous partial or complete fluorination of hydrocarbon molecules under
controlled conditions of temperature and concentration. Results from the
fluorination of neopentane are presented which indicate that although the
degree of fluorination for a given set of conditions indicates a gaussian
distribution, investigation of specific isomers indicate significant
deviations from statistical isomer distributions in fluorinated neopentanes.
Photochemical assisted fluorinations of neopentane, 1,4-dioxane, cyclohexane
and 2,2-dimethyl-1,3-dioxolane are described which produce the perfluorinated
analogs directly in good purity and in high yields.

The Low Temperature Fluorination of Aerosol
and Condensed Phase Sol Suspensions of Hydrocarbons
Utilizing Elemental Fluorine

Introduction

The fluorination of hydrocarbon molecules by present technology is limited to a few distinct methodologies. In most cases the most appealing methods from the standpoint of reaction rate and scale-up operate at elevated temperatures and produce generally lower yields of more complex molecules (Bigelow's "jet fluorination"); operate in anhydrous hydrogen fluoride which reacts with many organic moieties (Swart's Halogen Exchange Reaction and Simon's Electrochemical Process); utilize metal fluoride reagents which are expensive (AgF_2); or give incomplete fluorination with increasing complexity of the structure of the molecule to be fluorinated (CoF_3, $KCoF_4$). The low temperature direct fluorination process, on the other hand, is surface area dependent and utilizes mass transport to renew the surface of the solid phase hydrocarbon. Because the low temperatures slow the mass transport the reaction is unnecessarily slow although yields are usually quite high.

Our research is concerned with methods for producing and fluorinating at low temperatures fine uniform suspensions of solid particulates known as "sols." The method developed fluorinates "monodisperse" aerosol suspensions. The system described has the advantage of low temperature, solid phase, direct fluorination similar to the LTG process of Lagow, et. al. but is not dependent on low temperature mass transport to renew the reactant surface. This means that the reactions go in high yields and at an optimum rate limited by effective heat dissipation not mass transport.

Several of the above methods for the fluorination of hydrocarbons are

currently in commercial use. Each has varying advantages and disadvantages depending on the hydrocarbon and the functional group being fluorinated.

The Swarts reaction and other reactions involving halogen exchange require the preparation of the corresponding chlorocarbon derivatives prior to fluorination. Also fluorination becomes more difficult with increasing hydrogen or fluorine content on the carbon being fluorinated.[1] Higher perchlorocarbons than the methanes and ethanes are difficult to prepare and have reduced reactivity. These factors are serious limitations for complex molecules where the chloro derivatives are not only difficult to prepare, but perfluorination or removal of all chlorines on a hydryl derivative requires more reactive reagents such as mercuric or silver fluorides.

The electrochemical fluorination method developed by Simons[2,3,4,5] works very well for amines some carboxylic and sulfonic acids but rearrangements and β-cleavage occur for many acid and ether derivatives causing decreased yields.[4] This method utilizes the electrolysis of hydrogen fluoride solutions of hydrocarbon at an electrode potential lower than that capable of producing elemental fluorine. It is intrinsically simple and therefore commercially appealing. The major drawback is the instability of many functional groups in anhydrous hydrogen fluoride. Aldehydes, ketones and esters have not been successfully fluorinated in synthetically useful quantities using the electrochemical technique.

The cobalt trifluoride method pioneered by Fowler and coworkers[6] and other similar processes using high valent metal fluorides produce very good yields of saturated fluorocarbons with little fragmentation. The yields of F-alkanes produced by passing the vapor of n-alkanes over heated cobalt trifluoride were good but yields dropped sharply for more highly branched structures. A continuous reactor utilizing this process was designed and operated by these workers which produced F-alkanes and perfluorinated

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lubricating oils. The primary limitations of this process are the need to recycle and regenerate the spent metal fluoride (CoF_2) using elemental fluorine; the inability to completely fluorinate many compounds especially those with highly branched structures;[7] and the inability to fluorinate many functional hydrocarbons.

Fluorination with elemental fluorine has generally developed into two distinct methodologies. The "Jet Fluorination" technique developed by Bigelow and coworkers[8,9,10] utilizes gaseous reactants in separate streams, rapid mixing, and then quick removal of products from the reaction zone to reduce fragmentation. The other method developed by Lagow and Margrave[11,12,13] utilizes "long" reaction times and the high dilution of fluorine with helium which also acts as a heat sink. A later development in this process by Lagow, Maraschin and Adcock[14,15,16,17,18] couples the high dilution and "long" reaction time with a low-temperature (LTG) reactor densely packed with "light" copper turnings. This method produces good yields of highly branched fluorocarbons[14,15] and is generally useful for the fluorination of hydrocarbon ethers,[16] esters,[17] acid fluorides[17,18] acid anhydrides[19] and cyclic amines.[20] The method shows some potential for other functional groups, such as primary amines and ketones. It, however, works well only for molecules with appreciable solid state volatility and crystallinity. Materials that form oils, glasses or have low solid state volatility give considerably lower yields than the 30-80% yields obtained when more nearly ideal molecules are fluorinated. It is also a batch process which is generally suitable only for small scale syntheses.

All of the previously mentioned methodologies have serious limitations and although some have been adopted for industrial scale production, clearly a simple, more nearly general fluorination method would be desirable. We would like to present what we believe is such a method.

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Description of the Process

The significant successes of the LTG direct fluorination technique and the intrinsic simplicity of direct fluorination has led to a firm belief that a successful, general fluorination technique could be developed employing elemental fluorine. A critical analysis of the LTG reaction system produced a set of five conditions which we believe contribute to a high yield reaction. The conditions which we considered important are:

(a) Fluorination of molecules in the crystalline state.

(b) A very high reactant surface area exposed to gaseous fluorine.

(c) Low initial temperatures.

(d) High initial dilution of fluorine gas.

(e) A highly efficient mechanism of heat dissipation.

The crystalline matrix reduces hydrocarbon radical recombinations when radicals are formed under "dilute" conditions. The crystalline matrix acts as an energy sink to dissipate reaction energies. A high reactant surface area promotes uniform attack by fluorine on all reactant molecules. Low temperatures reduce the vigor of reaction by an overall reduction in kinetic energy and by limiting the number of radical chain initiations. High initial dilution of fluorine reduces the overall reaction rate and reduces the likelyhood of simultaneous attack by two fluorine molecules or radicals on adjacent sites on a molecule which would increase the degree of fragmentation. Effective heat dissipation would prevent the formation of "hot spots" and prevent combustion from occurring.[21]

These conditions, however, must be modified if one is to achieve high degrees of fluorination over a reasonable time span. The concentration of fluorine must be increased to maintain a good reaction rate as the reactant molecules become more highly fluorinated and a greater percentage of collisons are ineffective. It is also beneficial in this regard to increase

the temperature. Since these conditions directly conflict with the desired initial conditions their imposition must be separated in time or in space. The LTG system simply changes the applied temperature gradient and increases the fluorine concentration over time.

Separation of the perfluorination enhancing conditions from the initial conditions in space requires that the reactant be mobile. This mobile species may then be induced to pass through progressively warmer regions which have higher degrees of fluorine concentration. A gaseous reactant would be mobile, of course, but the desirability of limiting collisions between hydrocarbon radicals and thus limiting coupling reactions giving tars and oils dictates a condensed, preferably crystalline, phase. A liquid reagent stream does not allow for the uniform, rapid mixing of the very reactive gaseous elemental fluorine thus preventing uniform, controlled attack and substitution of fluorine at every C-H bond.

In order to achieve gas-like mobility and retain crystallinity it is necessary to produce extremely small solid particulates. These particulates may then be suspended and transported using a carrier gas. These particulates possess extremely high surface area which permits uniform attack by gaseous elemental fluorine on the suspended reactant. Extremely effective heat dissipation may be achieved by using helium as the carrier. Multiple collisions of the reactant particulates with the helium carrier gas molecules dissipate heat rapidly. Excess energy is continuously carried by the helium atoms to the walls of the reactor.

Principles of aerosol production are well developed. Our initial design ideas were developed from study of existing technology for producing aerosols which were developed primarily as an adjunct of atmospheric and industrial hygiene studies. Descriptive passages by N. A. Fuchs and A. G. Sutugin,[22] R. D. Cadle[23] and F. C. Goodrich[24] describe the requirements of generators

capable of producing aerosols. A more recent paper by A. G. Sutugin describes a mixer type generator which is generally applicable to the problem of steady state aerosol production in a flow reactor.[25] The major difference between our own independently developed design and that described by Sutugin is the subambient temperature capability of our design and its incorporation into a flow type reactor system.

The aerosol fluorination system designed to produce a controlled, continuous stream of aerosol particulates includes the following components (Figure 1). A bed of sodium fluoride heated to 850°C (A) sublimes highly dispersed NaF particles (average radius; 17.5 Å.[26]) into the helium carrier gas. These particles serve as condensation nuclei for the hydrocarbon condensation. The carrier gas is chilled to near -196°C by passing through a liquid nitrogen cooled heat exchanger (B). The chilled carrier gas, helium in this embodiment, is mixed with a second gas stream containing the hydrocarbon vapor in a precise arrangement within the body of the generator (C). The hydrocarbon vapor in the stream produced by an evaporator device (D) will condense into aggregates around the sodium fluoride particles within the chilled carrier. The chilled aerosol is directly channeled into the reactor (E) where it is mixed with elemental fluorine in such a way as to produce uniform contact between the aerosol particles and elemental fluorine. The temperature of the reactor (E) is controlled by means of an integral heat exchanger which can provide variable temperatures from the cryogenic to the ambient range.

The aerosol generator system is of the evaporation-condensation type. It, however, seems likely that aerosol particulates generated by any mechanism; physical, chemical or mechanical; would work equally well. It is the high surface area created by extensive subdivision of aggregates that is essential to the process.

FIGURE 1

AEROSOL FLUORINATOR

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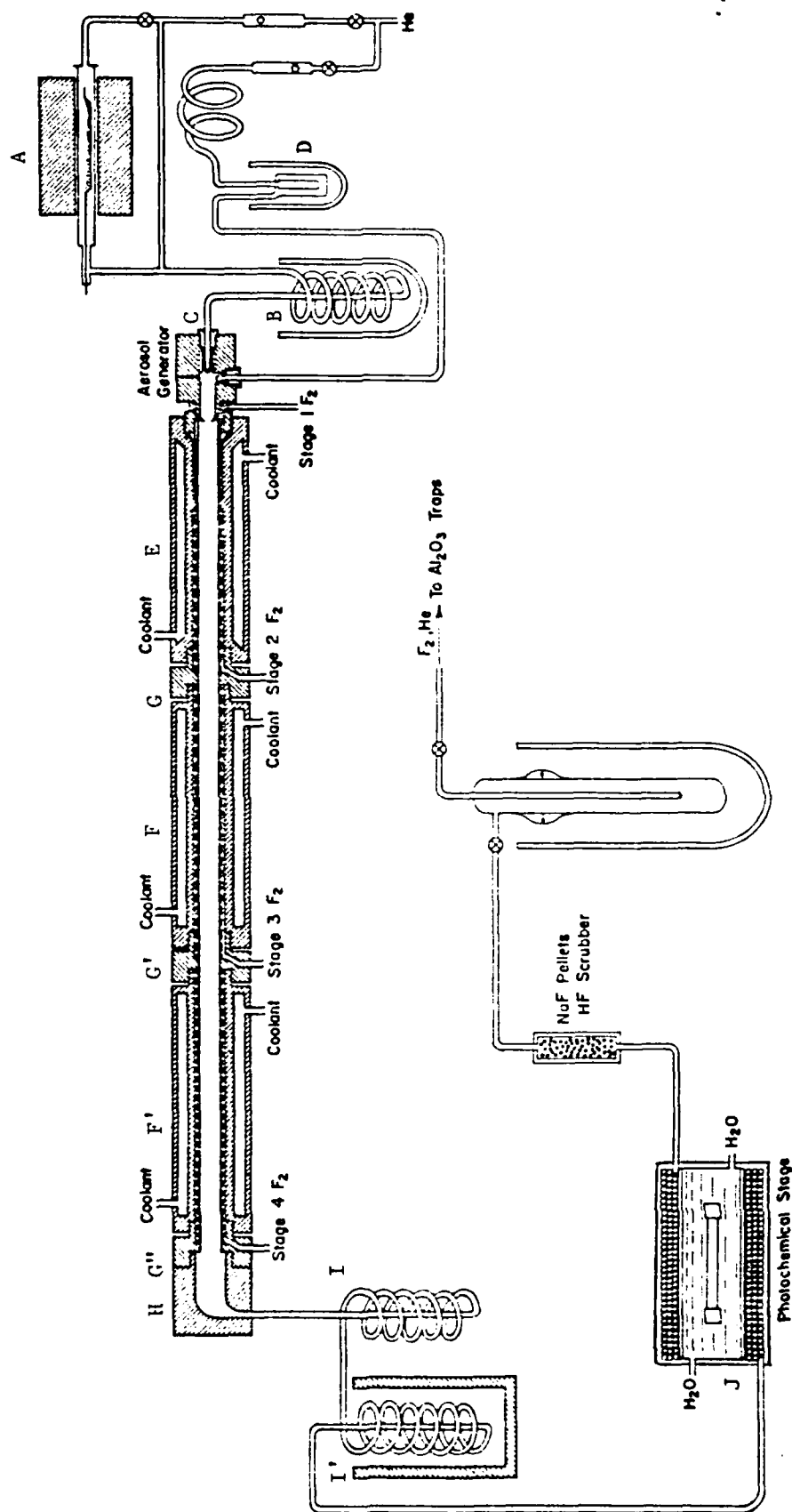
Having created a mobile reactant it is possible to separate in space the conditions giving low fragmentation, i.e., high initial dilution of fluorine, low temperature; from those conditions leading to high degrees of fluorination; i.e., increased fluorine concentration and temperature.

Modular design of the system has allowed for the addition of staging components following the reactor (E). Each staging component consists of a module (F) and a "staging insert," (G). A series of modules (F') connected to the reactor thus provide for independently controlled temperature zones and the addition of "staging inserts," (G') which allow the independently controlled injection of additional elemental fluorine. Using these devices hydrocarbon or other molecules may be controllably fluorinated to any degree including perfluorination. It is also conceivable that other reagents besides elemental fluorine can be introduced in the later stages to achieve functionalization, etc.[27-29]

The addition of modules and staging inserts may be continued indefinitely by insertion ahead of the end cap (H). Each stage may be modified to provide for recycling of any or all of the various reacting species although this is not practical at the lab scale. In the system shown (Figure 1) a total of three staging inserts have been assembled giving in effect a four-stage aerosol fluorination reactor in which fluorine can be added in four independently controlled zones at three independently controlled temperatures.[30]

In molecules which are exceptionally difficult to perfluorinate a heated coil (I') and/or a water cooled flow type photochemical reaction stage (J) following stage 4 (Figure 1) have been developed which significantly activate the elemental fluorine (or other reagent present in the reaction stream). The photochemical stage allows exceptionally high yields of perfluorinated products as well as much more efficient utilization of elemental fluorine.

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The multistaged aerosol fluorination reactor achieves optimum control over the potentially violent direct fluorination reaction. It is possible to expose the unfluorinated reactant to a very dilute, even distribution of elemental fluorine at low temperatures. Furthermore the condensed phase of the aerosol particle distributes reaction heat evenly over a large number of molecules held in an ideally crystalline aggregate which may readily dissipate energy by multiple rapid collisions with helium gas. All of these effects serve to reduce the violence and heat accumulation which are primary concerns in direct fluorination. As the reactant molecule becomes more highly fluorinated and hence less vulnerable the aerosol aggregate is carried into regions of higher fluorine concentration, higher temperature and generally more rigorous conditions which tend to bring about higher degrees of fluorination. Finally the highly fluorinated product mixture may be introduced into the photochemical stage to achieve maximum fluorination.

This combination of conditions, which allows independent control of reactant concentration, stoichiometry, temperature and reaction time, is unique to the aerosol fluorination reactor. It is in effect a dynamic, variable-fluorine-concentration-gradient, variable-temperature-gradient reactor.

Description of the Experiments

Neopentane was purchased from K and K Laboratories, Inc. and was used as received. 1,4-Dioxane and Cyclohexane (Fisher) were dried over Linde 4-A molecular sieve before used. 2,2-Dimethyl-1,3-dioxolane was prepared by allowing a 1:2 molar mixture of acetone:ethylene glycol to reflux over L-4A molecular sieve in the presence of paratoluene sulfonic acid for several days. The filtered liquid was run slowly into saturated aqueous patassium carbonate. The separated organic (top) layer was dried over L-4A sieves and

fractionally distilled using a spinning band distillation apparatus. The pure product (b.p. 89.0-90.0°C, Lit[31] 90.0°C) was collected in 11% yield although much more was collected as an apparent acetone azeotrope.

Elemental fluorine was purchased from Air Products Co. (97% Technical Grade, low oxygen content) in a cylinder containing 4.9 lbs F_2 at 400 psig. IR spectra were run on a Perkin Elmer 257 grating spectrophotometer; Mass Spectra (Electron Impact and Chemical Ionization) were obtained on a Hewlett Packard 5980A Mass Spectrometer. ^{1}H and ^{19}F NMR were obtained from the South Carolina Magnetic Resonance Facility, Columbia, South Carolina, operating under NSF-CHE78-18723. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Mass throughput values for neopentane 1,4-dioxane, 2,2-dimethyl-1,3-dioxolane and cyclohexane were calculated from empirical data which are presented in Table 1. Reactions with neopentane throughput at 4 mmoles per hour were run with the neopentane reservoir (D) at -63°C, He flow 101cc/min, throughput 0.29 g/hr, 4.0 millimoles/hr. Gas chromatographic separations were made on a Bendix Model 2300 gas chromatograph with multilinear programing and TC detection. The photochemical reaction stage consisted of ten meters of 0.015" wall, 3/8" ID FEP Teflon Tubing wrapped one layer around a 50mm x 390mm quartz immersion well containing a 550 watt (Hanovia) medium pressure mercury arc lamp and a second layer wrapped concentrically about an overlying 75mm pyrex tube. All FEP teflon tubing is maintained at approximately 20°-25°C by positive water circulation over all surfaces.

Neopentane Reactions: F/N-1 through 7 were run on the two stage modification of the aerosol reactor designated (S). This reactor consisted of the reactor with stage two insert, one staging module without insert followed by the end piece, H, and connecting tubing (3/8" copper tubing). The active volume of this reactor was 321 cm^3 with average diameter of less than 0.5

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inch. Reaction conditions are compiled in Table 2. Reaction times were approximated by dividing the active volume of the reactor by the combined flows of gas, principally helium.

Reactions F/N-8 through F/N-12 were run on the four stage modification of the aerosol reactor designated (T). This reactor consisted of the reactor with stage two insert, two staging modules each fitted with staging inserts followed by the end piece and connecting tubing. The active volume of this reactor was 268 cm^3. The reduced volume is a result of the volume displacement by the second staging insert in the first staging module present in (S). Reaction conditions are compiled in Table 3.

Reactions F/N-13 through F/N-21 were run on the four stage modification (T) extended by the addition of a ten meter x 3/8" copper coil which increased the active volume of this reactor designated (U) to 771 cm^3. A fifteen meter coil of 3/8 inch copper tubing [reactor designate (V)] and/or the photochemical module [reactor designate (W)/(X)] pictured in Figure 1 were the final extensions increasing the active volumes to 1524 cm^3, 2108 cm^3 or 1355 cm^3 respectively. Their effect on reaction times are proportional to the volume changes however their effects on product distributions are not nearly so marked as that produced by the first coil but improvement does occur (UV off). Reaction conditions for reactor modification designate (U) are compiled in Table 4.

The left part of each table of reaction conditions (e.g. Table 4) lists the experimental values for the different variables used in a given reaction. These are: a) the flow of hydrocarbon, b) the flow of fluorine and c) the flow of inert gas, which consists of the main carrier, the hydrocarbon carrier and the fluorine diluent. Another variable, d) the temperature of the reactor, is only listed in the tables for the multistaging experiments, because it was kept constant at -65°C in all single-stage fluorination experiments.

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The right part of each table lists reaction parameters which were calculated from two or more of the variables previously listed. The hydrocarbon to fluorine (h.c.: F_2) ratio needs no explanation.

The "stoichiometry" listed in the next column(s) is the fluorine-to-hydrocarbon-ratio divided by the number of hydrogens on the hydrocarbon molecule considered. This is more useful than the fluorine-to-hydrocarbon-ratio itself, for example:

1. To completely substitute one hydrocarbon molecule with $\underline{n}$ hydrogen atoms $\underline{n}$ F_2-molecules are needed for complete fluorination.

2. If different hydrocarbons are compared, the "stoichiometry" gives a better picture of the true reaction conditions than the F_2:h.c.-ratio itself. For example, a 24:1 F_2:h.c.-ratio means a twofold excess of fluorine if cyclohexane or neopentane are considered (stoichiometry = 24:12 = 2), but a threefold excess of fluorine in the case of 1,4-dioxane (stoichiometry = 24:8 = 3).

The next column of each table lists the fluorine concentration for each reaction. This was calculated from the overall fluorine flow divided by the sum of all flows going through the reactor (x100). Thus it represents the concentration one would find at the end of the reactor (in multistaging experiments at the end of module #2), if no reaction would occur. The true fluorine concentration is certainly lower than this value, the error being larger for reactions with high hydrocarbon flows and low fluorine flows, while in reactions with low hydrocarbon throughputs and large excess of fluorine the true F_2-concentration is probably close to the value listed. In multistaging experiments a gradient in fluorine concentrations was used. For some of the reactions an approximate fluorine concentration profile is given in the diagrams (Figures 2-7) for the product distributions of neopentane fluorinations.
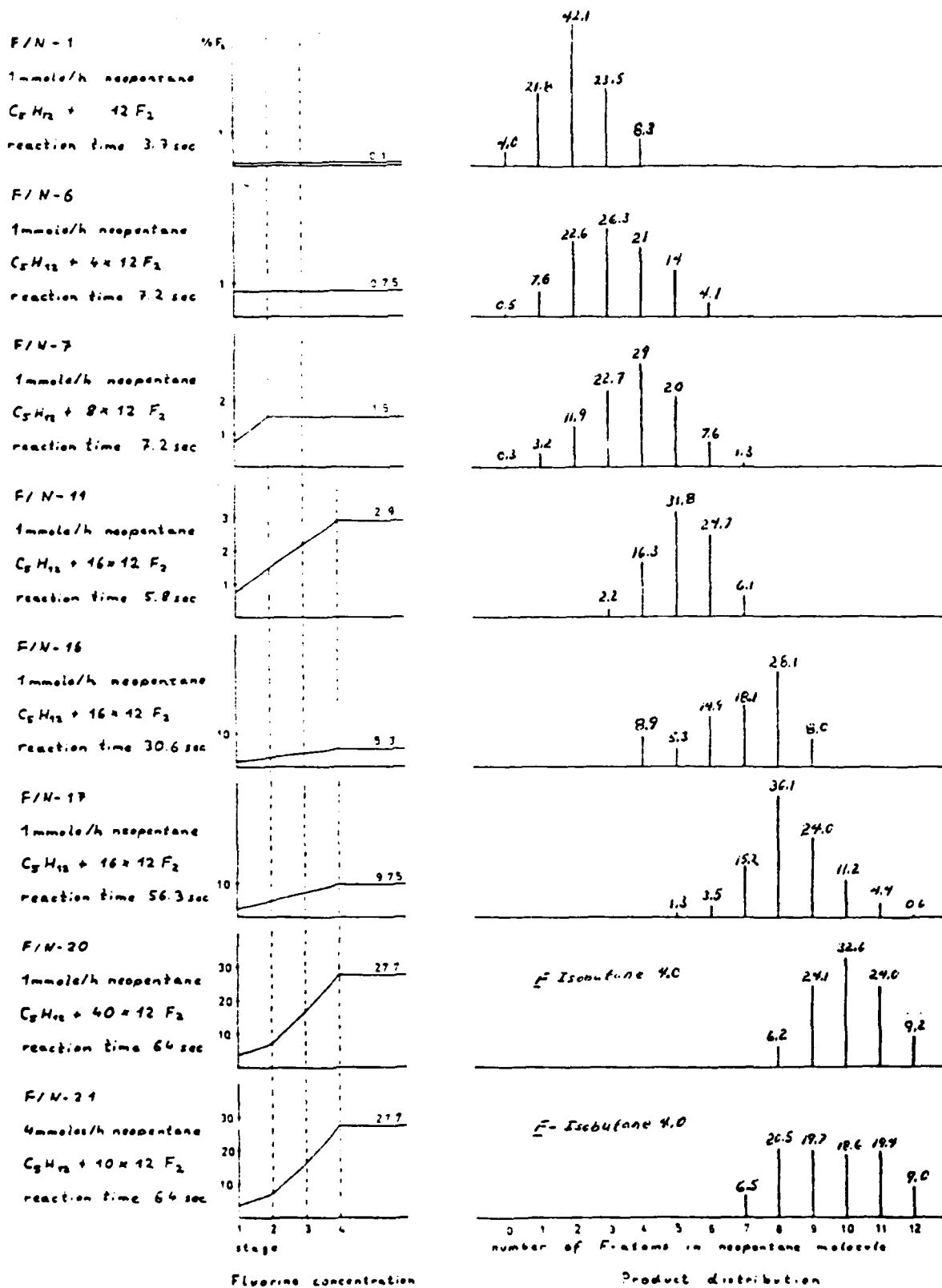
13

FIGURE 2

NEOPENTANE PRODUCT DISTRIBUTIONS

F/N - 1   %F₂

1 mmole/h neopentane

C_5H_{12} + 12 F_2

reaction time 3.7 sec

0.1

4.0   21.6   42.1   23.5   8.3

F/N - 6

1 mmole/h neopentane

C_5H_{12} + 4 × 12 F_2

reaction time 7.2 sec

0.75

0.5   7.6   22.6   26.3   21   14   4.1

F/N - 7

1 mmole/h neopentane

C_5H_{12} + 8 × 12 F_2

reaction time 7.2 sec

1.5

0.3   3.2   11.9   22.7   29   20   7.6   1.3

F/N - 11

1 mmole/h neopentane

C_5H_{12} + 16 × 12 F_2

reaction time 5.8 sec

2.9

2.2   16.3   31.8   24.7   6.1

F/N - 16

1 mmole/h neopentane

C_5H_{12} + 16 × 12 F_2

reaction time 30.6 sec

5.3

8.9   5.3   14.5   18.1   26.1   8.0

F/N - 17

1 mmole/h neopentane

C_5H_{12} + 16 × 12 F_2

reaction time 56.3 sec

9.75

1.3   3.5   15.2   36.1   24.0   11.2   4.4   0.6

F/N - 20

1 mmole/h neopentane

C_5H_{12} + 40 × 12 F_2

reaction time 64 sec

27.7

F = Isobutane 4.0

6.2   24.1   32.6   24.0   9.2

F/N - 21

4 mmoles/h neopentane

C_5H_{12} + 10 × 12 F_2

reaction time 64 sec

27.7

F = Isobutane 4.0

6.5   26.5   19.7   18.6   19.4   9.0

1   2   3   4   stage

0 1 2 3 4 5 6 7 8 9 10 11 12

number of F-atoms in neopentane molecule

Fluorine concentration

Product distribution

14

FIGURE 3

NEOPENTANE PHOTOCHEMICAL PRODUCT DISTRIBUTIONS

PF/N-1

2 mmol/hr C_5H_{12}

2.6 mmol/hr F_2

PF/N-2

2 mmol/hr C_5H_{12}

4.8 mmol/hr F_2

PF/N-3

2 mmol/hr C_5H_{12}

12 mmol/hr F_2

PF/N-4

2 mmol/hr C_5H_{12}

24 mmol/hr F_2

PF/N-5

2 mmol/hr C_5H_{12}

24 mmol/hr F_2

PF/N-6

4 mmol/hr C_5H_{12}

96 mmol/hr F_2

PF/N-7

1 mmol/hr C_5H_{12}

480 mmol/hr F_2
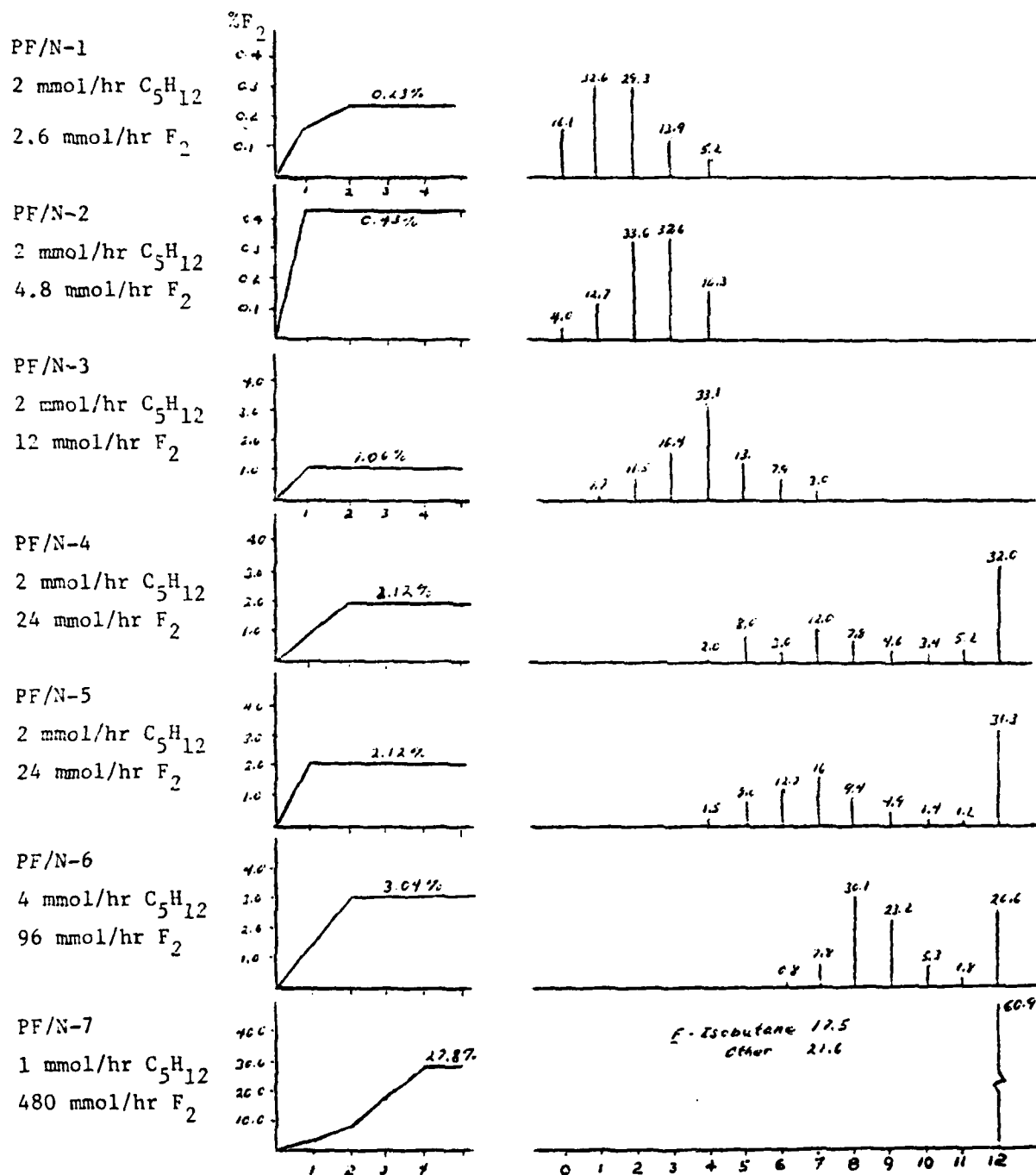
FIGURE 4

NEOPENTANE PRODUCT DISTRIBUTION

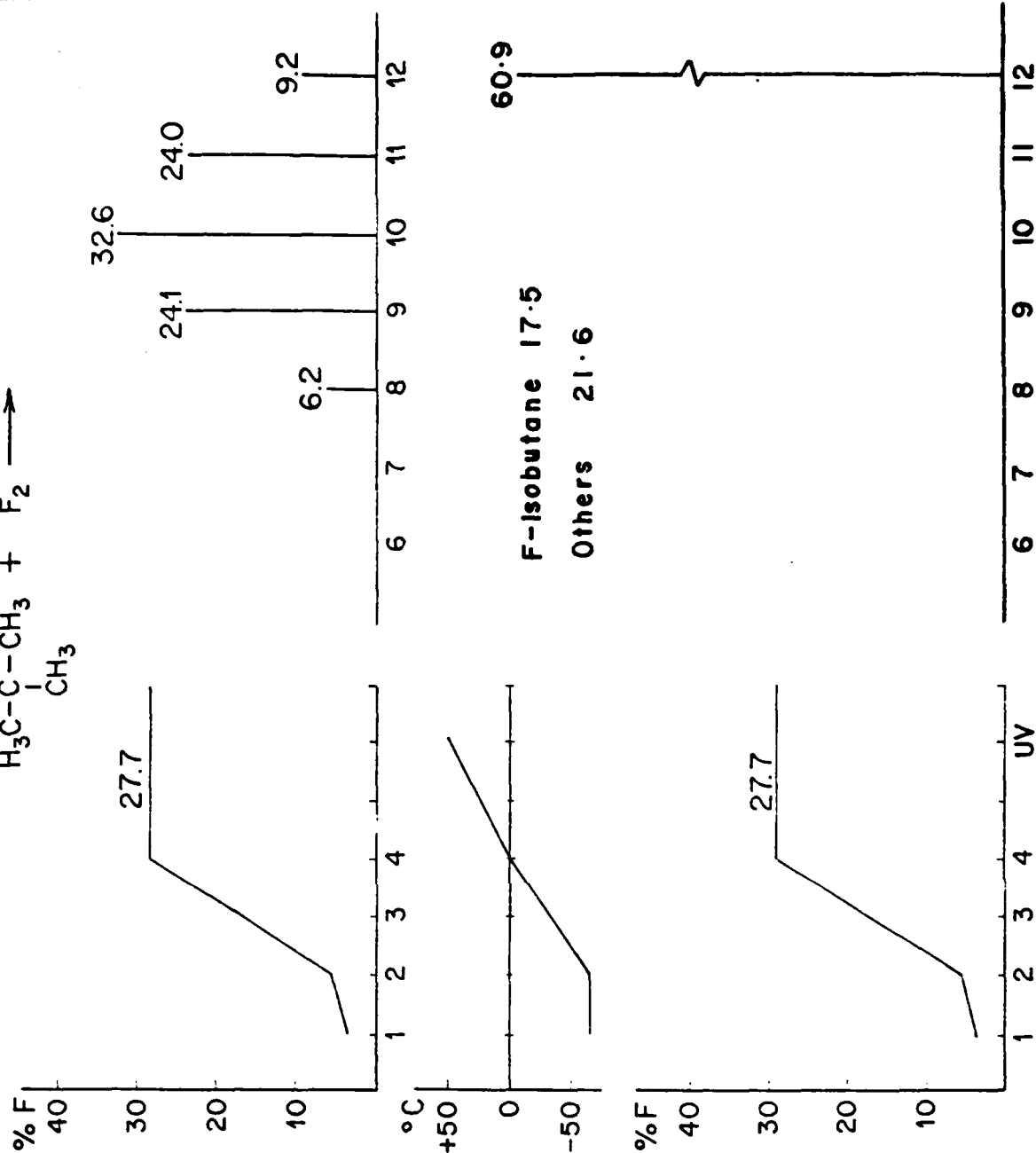$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3 + F_2 \longrightarrow$$
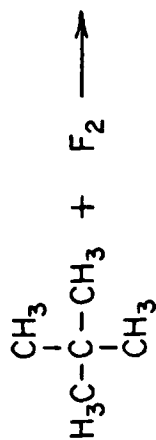
F/N-20

Hydrocarbon: 1.0 millimole/hour

Fluorine: 480 millimole/hour

$C_5H_{12} + 40 \times 12F_2 \xrightarrow{\text{64 sec}}$

Temperature Gradient

With Ultraviolet Stage:
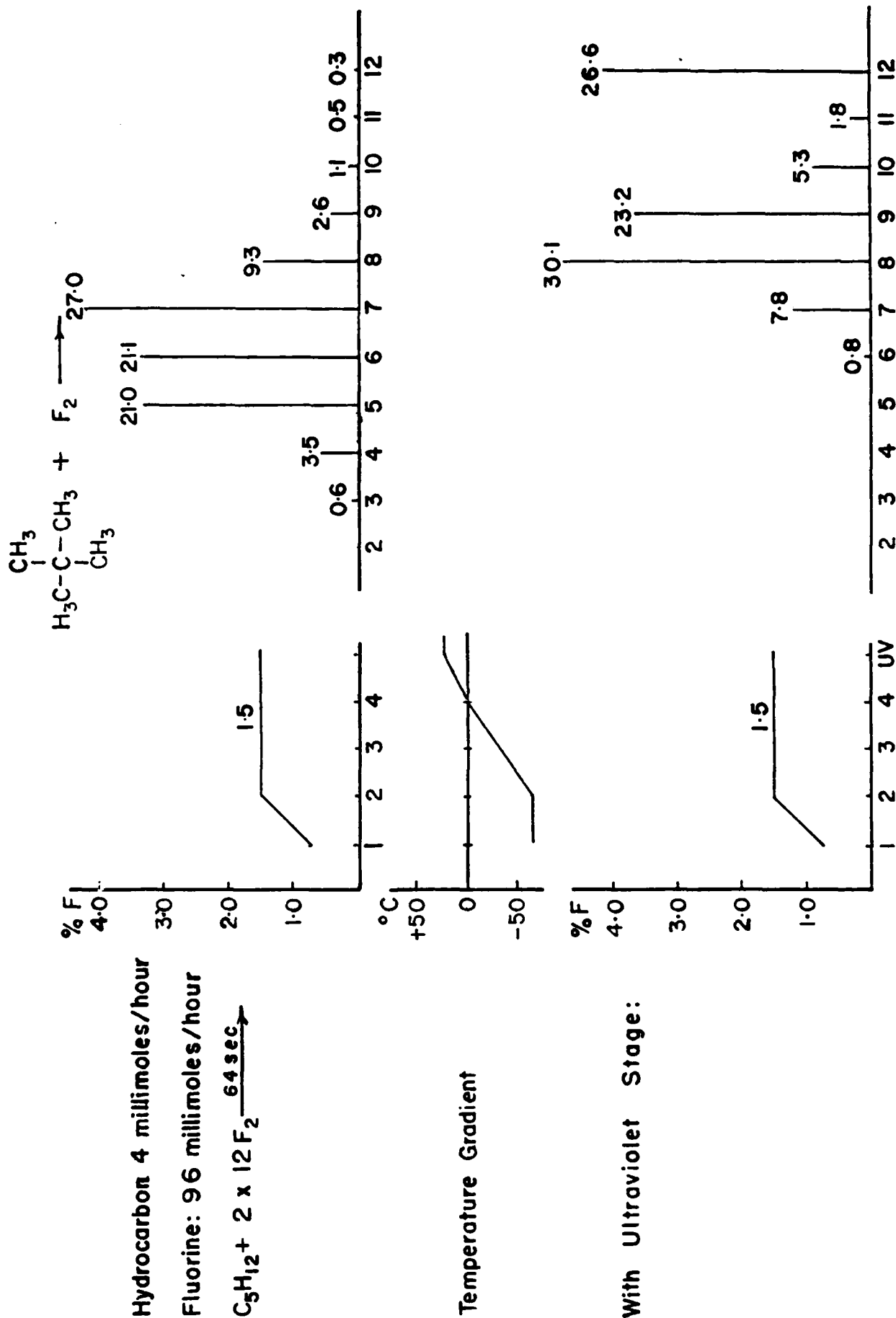
F-Isobutane 17·5

Others 21·6
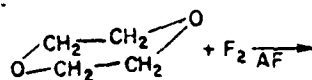
FIGURE 5

NEOPENTANE PRODUCT DISTRIBUTION

FIGURE 6

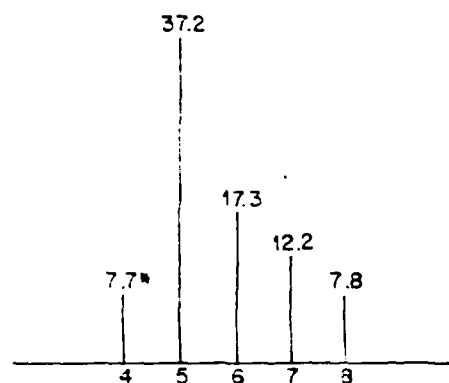## 1,4 – DIOXANE PRODUCT DISTRIBUTION

F/D – 12

Hydrocarbon: 1.0 millimole/hour

Fluorine: 480 millimole/hour

$C_4H_8O_2 + 60 \times 8F_2 \xrightarrow{\text{2.2 min}}$
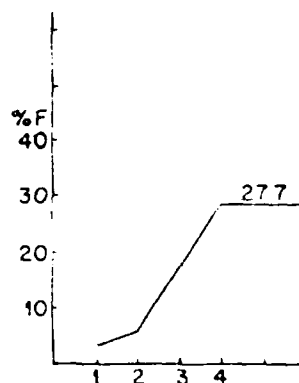
Temperature Gradient

* Lower 1,4–Dioxane isomers decompose readily by loss of HF and Hydrolysis.

Hydrocarbon: 2.0 millimole/hour

Fluorine: 480 millimole/hour

$C_4H_8O_2 + 30 \times 8F_2 \xrightarrow{\text{2.2 min}}$

With Ultraviolet Stage:
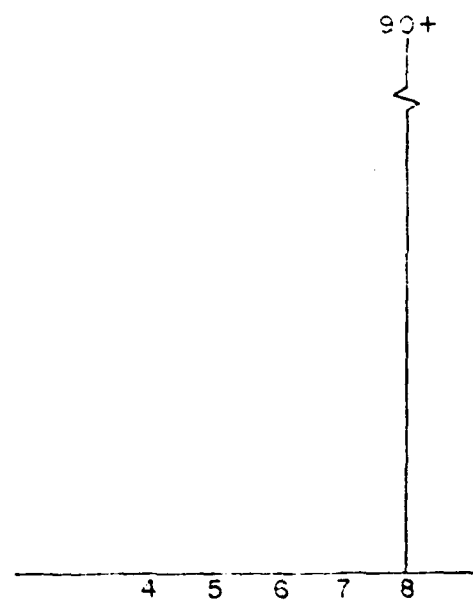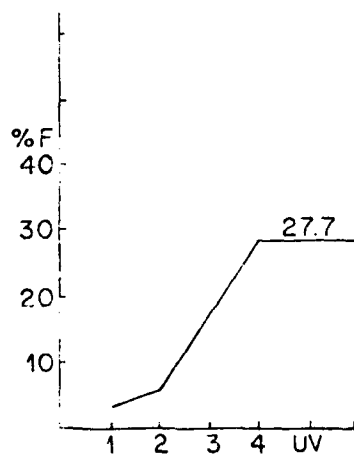
Temperature Gradient
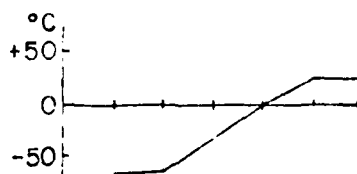
FIGURE 7

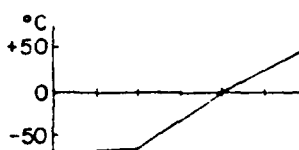# 2,2-DIMETHYL-1,3-DIOXOLANE PRODUCT DISTRIBUTION
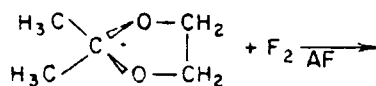
F/DD - 4

Hydrocarbon: 6.0 millimole/hour

Fluorine: 480 millimole/hour

$C_5 H_{10} O_2 + 48 \times 10 F_2 \xrightarrow{2.2\,min}$

%F

Temperature Gradient

°C

* Lower 2,2-Dimethyl-1,3-Dioxolane isomers decompose readily.

Hydrocarbon: 2.0 millimole/hour

Fluorine: 480 millimole/hour

$C_5 H_{10} O_2 + 24 \times 10 F_2 \xrightarrow{2.2\,min}$

With Ultraviolet Stage:

%F

Temperature Gradient

°C
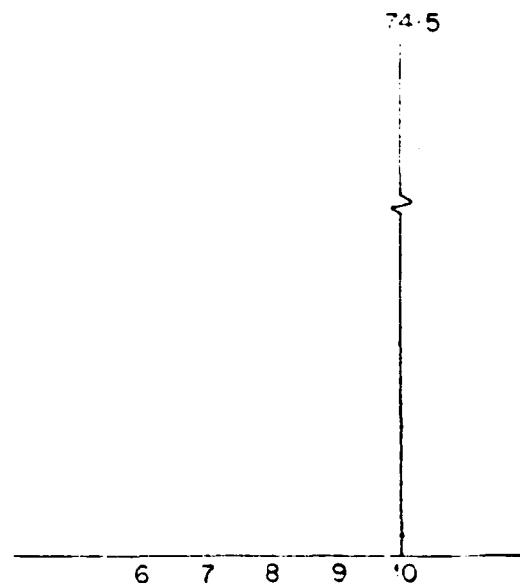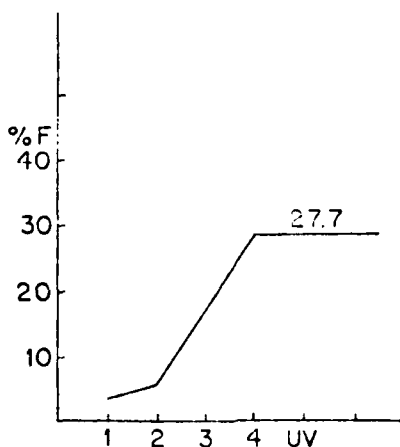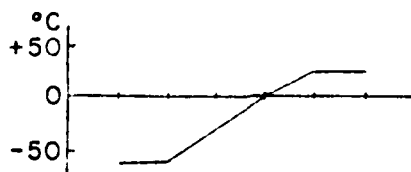
The last column of the tables for reaction conditions lists the reaction time. This means the average time a hydrocarbon particle travels from the aerosol generator to the product collecting trap, where it is frozen to -196°C and the reaction stops. This time was calculated from the volume of the reactor and the sum of flows through it. Of course this is only correct, if no hydrocarbon condenses inside the reactor at any time during a run. For the fluorinations of neopentane, especially those with high fluorine concentrations, this assumption is probably correct because of the high volatility of solid neopentane at -65°C.

Product mixtures from all neopentane fluorinations were treated with NaF/molecular sieves. To check the performance of every reaction, an analytical GLC-injection of a solution of the product mixture in CCl_4 was made on a 3/8" x 7 m fluorosilicone QF-1 column (Analabs). The temperature program used is the same as for product separations from LTG-neopentane fluorinations: T_1 = 25°C for 10 min; R_1 = 10°/min; T_2 = 75°C for 10 min; R_2 = 50°/min; T_3 = 125°C for 24 min.

To identify the unknown partially fluorinated neopentanes, products from reactions F/N-1, 11, 14, 17, 18 and 19 were separated preparatively by GLC to obtain samples for NMR-measurements (Tables 5 and 6). Corresponding products from reactions F/N-2, 4, 5 and 13 were separated for mass spectral investigations (Table 7).

Identical samples from the different reactions (as certified by IR) were combined to obtain sufficient material for spectral investigations and elemental analysis of some products since every two hour reaction run with a hydrocarbon flow of 1 mmole/h gave only 100 to 300 mg of crude product mixture.

Only one fraction from the first GLC-separations was further separated. The QF-1 peak between 33 and 35 min retention time (NF, NO, NP) was

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separated on a phenyl-methylsilicone rubber column SE-52 with the following temperature program: $T_1 = 70°C$ for 10 min; $R_1 = 25°/min$; $T_2 = T_3 = 120°C$ for 7 min. Compounds NS and NT occurred in some reactions as a difficult to separate mixture but could be produced nearly pure by stoichiometric control. All purified products prepared for elemental analysis were assayed on the SE-52 column to establish purity after initial QF-1 column GLC purification.

The product distributions for some typical reactions were estimated by determining the areas of peaks in the GLC-traces (Table 8). The reactions chosen for this were: F/N-1, F/N-6, F/N-7, F/N-11, F/N-16, F/N-17, F/N-20 and F/N-21. Table 8 lists these product distributions. Since no decomposition during work-up was observed, and all materials were volatile and soluble in CCl_4, these values should represent something close to the real product distribution for the neopentane fluorinations under different reaction conditions. Thus these distributions could be used to graphically show the effect of reaction parameters on fluorination efficiency. Compounds are ordered NA through NT on the basis of their Fluorosilicone QF-1 retention time (Table 9).

Photochemical Neopentane Reactions: Procedures for conducting the photochemical neopentane reactions were very similar to the "dark" reactions. As previously was the case, the particulate furnace, cooling jackets, carrier flows, fluorine flows and where used the photochemical cell were allowed to come to equilibrium-readiness before any hydrocarbon was admitted to the system. The details of the photochemical experimental conditions for neopentane [PF/N-1 through PF/N-7, reactor configuration (X)] are listed in Table 10. A set of control runs (NPF/N-4 through NPF/N-7) were run under identical conditions except the photochemical lamp was off. The product distributions of the control runs are illustrated along with the photochemical runs on Figures 4 and 5.

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The problems of mass balance in the aerosol system are complex. Through-puts are determined empirically by collecting the output of the hydrocarbon evaporator over several half hour periods. A calibration curve is developed as a function of carrier flow versus mass output for a given reservoir temperature. Except for those reactions giving only a few products, yields are tedius, time consuming and prone to experimentalist technique losses. Product distributions as given can be deceiving in that they are yields relative to other products. Generally output masses are about two thirds of those expected even when no fluorine is used. This points out one of the difficulties of aerosol particulates, i.e., their capture. Yields of the photochemical experiments leading to a few products are given. Reaction PF/N-7 yields 0.54g F-neopentane for a 5 hour, one millimole per hour run. Theoretical yield estimate 5 millimoles, 1.44g, a yield of 38%.

Products from the aerosol fluorinations of neopentane were identified on the basis of their ^{19}F (Table 5) and ^{1}H (Table 6) spectra, CI and EI mass spectra, elemental analysis and IR spectra (Table 7). Assignments are based mainly on the NMR spectra, because the chemical shifts for fluorines as well as hydrogens on the differently fluorinated methyl groups (i.e. CH_3, CH_2F, CHF_2, CF_3) are very characteristic; their couplings are relatively simple, and integrations also help to clearly identify products.

Mass spectral data for the partially fluorinated neopentanes are not conclusive, because (except for mono-fluoro- and difluoroneopentane) no molecular ion or molecular ion minus fluorine was found.

1,4-Dioxane Reactions: Although many reactions involving all levels of fluorination of 1,4-dioxane were performed,[30] the instability of the poly-fluoro-1,4-dioxanes, especially the trifluoro species, prevented as detailed an examination of product distributions as was detailed for neopentane. Only those reactions producing high degrees of fluorine substitution were

amenable to even near quantitative workup. For these later runs reactor
configuration (V) was used for the initial "dark" reaction runs and reactor
configuration (X) was used for the photochemical runs and their controls
(Table 11). In each case the products collected were condensed into a
reservoir containing sodium fluoride pellets and L-4A molecular sieves
separated by a one inch layer of "light" copper turnings and allowed to
stand at room temperature overnight. The products remaining were vacuum
line fractionated through -78°C, -131°C and -196°C traps. The -78°C and
-131°C traps were combined and subjected to gas chromatographic separation
on the fluorosilicone QF-1 column described earlier at a constant temperature
of 125°C. The -196°C trap, usually containing only a few milligrams of very
volatile material was discarded.

Products from the fluorinations of 1,4-dioxane have been characterized
by their ^{19}F and ^{1}H NMR spectra, CI and EI mass spectra and IR spectra. As
is also the case for partially fluorinated cyclohexanes, ^{1}H NMR spectra of
partially fluorinated 1,4-dioxanes are very complex due to coupling across
the ring. But again signals of CH_2 groups and signals of CFH-groups can be
clearly distinguished and their relative integrations give information about
the extent of fluorination. ^{19}F NMR spectra are somewhat simpler. In ad-
dition, ^{19}F NMR spectra for both the fully and partially fluorinated 1,4-
dioxanes containing four or more fluorine atoms have been described in
detail in the literature making characterization much simpler.[7,32]

Mass spectra of partially fluorinated 1,4-dioxanes are also very useful
for identification; EI mass spectra usually show $C_2F_nH_{4-n}$-masses with very
high intensities, from which the number of fluorine atoms on each side of the
ring can be determined. This information allowed the product distribution
graphs to be readily constructed for reactions involving the more highly
fluorinated 1,4-dioxanes that may be cleanly separated by single glc

injection (Figure 6). Reaction PF/D-1 produced 0.7963g of F-1,4-dioxane for a 3 hour-2 millimole per hour run. Theoretical yield estimate for 6 millimoles F-1,4-dioxane is 1.33g a yield of 57%.

Cyclohexane Reactions: Again many reactions at virtually all levels of fluorination were conducted with cyclohexane.[30b] The highly complex ^{1}H and ^{19}F NMR spectra due to extensive coupling and conformational equilibria have been to a great extent worked out in the literature.[33-35] The difficulty in providing meaningful product distributions arises from the difficulties in obtaining quantitative separation of the various products which required use of up to three, generally two, different glc columns on each complex fraction. For this reason only the photochemical results for conditions leading to perfluorination are reported (Table 11). The product collected was almost pure F-cyclohexane in 30% yield based on the average throughput of two millimoles per hour.

2,2-Dimethyl-1,3-dioxolane Reactions: Only reactions leading to high degrees of fluorination are listed in Table 11. Characterization of various hydryl-F-2,2-dimethyl-1,3-dioxolanes, are given in the literature.[36] The product distributions (Figure 7) represent only those seven major components (∿70% total) which are "stable" to the NaF/L-4A treatment and do not pass a -131°C trap at 10^{-3} torr. The product distributions (Figure 7) are estimates based on gas chromatographic assay on Fluorosilicone QF-1 using the temperature separation program T_1 = -8°C for 8 min; heating 8°C/minute, T_2 = 144°C for 20 minutes. The photochemical fluorination resulted in collection of 1.1593g of material at an average hydrocarbon throughput of 2 millimoles per hour for three hours. GLC purification of the product gave 0.87g (74.5%) pure F-2,2-dimethyl-1,3-dioxolane resulting in a yield estimate of 51.4%.

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Results and Discussion

Neopentane, 1,4-dioxane, cyclohexane and 2,2-dimethyl-1,3-dioxolane have all been successfully fluorinated by the aerosol process. Neopentane, however, was chosen as the model compound for detailed study of the reactor system for several reasons. Five of the most important reasons are enumerated below:

i) Partially fluorinated neopentanes are stable, since elimination of HF, which is very favorable in partially fluorinated dioxanes and dioxolanes, cannot occur; γ-elimination of HF to form a 3-membered ring should not occur under work-up conditions.

ii) Partially fluorinated neopentanes have a higher volatility and solubility in CCl_4 than similar fluorinated cyclohexanes or dioxanes, thus facilitating work-up and giving a more accurate product distribution.

iii) There are not as many different isomers. Also different conformations for a given degree of fluorination such as occur in dioxane or cyclohexane are not a problem. Therefore the influence of reaction parameters should be more easily seen directly from the product distribution.

iv) Gas chromatographic separation in one step has proved to be possible, so that the GLC-chromatogram could be used for quantitative estimation of product distributions.

v) Four of the most highly fluorinated neopentanes (i.e. F-neopentane, undecafluoroneopentane, decafluoroneopentane and nonafluoroneopentane) were known from gradient reactor reactions, thus making it easier to judge the "success" of a fluorination.[14,37]

Initially twenty-one non-photochemical reactions with neopentane were run and the results compared. In each of these reactions variables such as carrier flow, fluorine concentration gradient, reaction time and hydrocarbon mass throughput were changed. Repetative runs were made, generally only one

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variable at a time was changed so as to ascertain its effect on product distributions. In none of the cases outlined in Tables 2-4 was the reactor or reaction uncontrolled or perceptively violent even in those runs involving fluorine flows exceeding 200 cc/minute (480 mmoles/hr). The product distributions for neopentane as a function of the fluorine concentration gradient in these initial runs are given in Figure 2. In this diagram isomers are combined to illustrate the degree of fluorination obtained as a function of fluorine concentration, concentration gradient, relative F_2:h.c. stoichiometry and reaction time. It is quite evident that a gaussian distribution of products is approached. This is seen most clearly in reactions F/N-1, F/N-11, F/N-17 and F/N-20. Significant deviations however occur for certain sets of conditions. The most readily explicable is that illustrated by F/N-21, Figure 2. In this reaction only the hydrocarbon throughput was increased (four-fold) relative to F/N-20. This effect, a compression of the maximum toward lower substitution, is undoubtedly due to fluorine concentration gradient changes as the increased hydrocarbon throughput consumes additional fluorine. The molar amount of fluorine is not at every point much greater than the molar amount of hydrocarbon. This effect is reproducible.

Preferential Fluorine Reactivity

The preceding discussion indicates that fluorination occurs stepwise under our conditions and that product distributions with regard to degree of fluorination should be readily explainable on simple statistical and kinetic grounds. The question which remains is whether each degree of fluorination exhibits a distribution of isomers based on simple statistics. In this regard it became necessary to identify each possible isomer, its statistical weight based upon the assumption of stepwise fluorination, and the comparison of the theoretical with the experimental distribution of

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isomers. Because of the nature of the aerosol process, the assumption that only effects due to statistical weighting or internal directive effects should be important is a defendable one. The basic process involves finely dispersed hydrocarbon particulates in a gaseous helium matrix which are subjected to diffusion controlled attack by gaseous fluorine. Fluorine is injected evenly along the reactor length so as to produce a dynamic fluorine concentration gradient which is ideally at a steady state. Fluorine concentration should remain constant at any given point along the reactor length. This unique set of conditions roughly approximates the conditions produced by a molecular beam apparatus where two reactants intersect and react in a manner governed by condition dependent statistical probability as operated on by the intrinsic reactivities of the reactants themselves. In the aerosol system the intersecting points are random; diffusion controlled, and compound permitting only a statistical treatment and an approximate one at that. It should however be possible to achieve a qualitatively valid comparison between experiment and theory.

For this comparison the products of eight selected reactions of neopentane with elemental fluorine were separated by gas chromatography, and analysed by ^{1}H and ^{19}F nmr and EI and CI mass spectrometry. The isomer distributions are based on relative peak areas of the thermal conductivity chromatograms.

The statistical probability of isomers based on the assumption of stepwise substitution are illustrated in Figure 8. In Figure 8 the statistical probability of each isomer based on stepwise substitution is indicated. In each case the probability of the most symmetrical isomer is underlined. The experimentally determined isomer distribution (which is the average of three to five reactions) was determined by comparison of relative peak areas of the gas chromatographed products. In all cases the most unequivocal

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Figure 8

The Statistical Probability of Isomers Based on Stepwise Substitution of Hydrogens by Fluorine

Monofluoroneopentane:

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2F}{|}}{C}}-CH_3$$

Statistical Probability: 1.000
Experimental Distribution:

Difluoroneopentanes:

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2F}{|}}{C}}-CH_2F \quad + \quad H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CHF_2}{|}}{C}}-CH_3 \rightarrow$$

$$\underline{0.8182} \qquad\qquad 0.1818$$
$$0.8991 \qquad\qquad 0.1157$$

Trifluoroneopentanes:

$$H_3C-\underset{\underset{CH_2F}{|}}{\overset{\overset{CH_2F}{|}}{C}}-CH_2F \quad + \quad H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CHF_2}{|}}{C}}-CH_2F \quad + \quad H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CF_3}{|}}{C}}-CH_3$$

$$\underline{0.4909} \qquad\qquad 0.4909 \qquad\qquad 0.0182$$
$$0.5925 \qquad\qquad 0.4075 \qquad\qquad \text{--}$$

Tetrafluoroneopentanes:

$$FH_2C-\underset{\underset{CH_2F}{|}}{\overset{\overset{CH_2F}{|}}{C}}-CH_2F \quad + \quad H_3C-\underset{\underset{CH_2F}{|}}{\overset{\overset{CHF_2}{|}}{C}}-CH_2F \quad + \quad H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CHF_2}{|}}{C}}-CHF_2 \quad +$$

$$\underline{0.1636} \qquad\qquad 0.6545 \qquad\qquad 0.1091$$
$$\underline{0.1411} \qquad\qquad 0.8344 \qquad\qquad 0.0245$$

$$H_3C-\underset{\underset{CH_2F}{|}}{\overset{\overset{CF_3}{|}}{C}}-CH_2F$$

$$0.1364$$
$$\text{--}$$

Pentafluoroneopentanes:

$$FH_2C-\underset{\underset{CH_2F}{|}}{\overset{\overset{CHF_2}{|}}{C}}-CH_2F \quad + \quad H_3C-\underset{\underset{CH_2F}{|}}{\overset{\overset{CHF_2}{|}}{C}}-CHF_2 \quad + \quad H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CF_3}{|}}{C}}-CHF_2 \rightarrow$$

$$\underline{0.4091} \qquad\qquad 0.4091 \qquad\qquad 0.0455$$
$$\underline{1.0000} \qquad\qquad \text{--} \qquad\qquad \text{--}$$

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CF_3}{|}}{C}}-CH_2F$$

$$0.0727$$
$$\text{--}$$

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Figure 8 (Continued)

Hexafluoroneopentanes:

$$
\underset{\substack{\text{0.5260}\\\overline{\text{1.0000}}}}{\underset{\text{CH}_2\text{F}}{\overset{\text{CHF}_2}{\text{FH}_2\text{C}-\text{C}-\text{CHF}_2}}}
+
\underset{\substack{\text{0.2338}\\\text{--}}}{\underset{\text{CH}_2\text{F}}{\overset{\text{CF}_3}{\text{H}_3\text{C}-\text{C}-\text{CHF}_2}}}
+
\underset{\substack{\text{0.1169}\\\text{--}}}{\underset{\text{CHF}_2}{\overset{\text{CHF}_2}{\text{H}_3\text{C}-\text{C}-\text{CHF}_2}}}
+
\underset{\substack{\text{0.1169}\\\text{--}}}{\underset{\text{CH}_2\text{F}}{\overset{\text{CF}_3}{\text{FH}_2\text{C}-\text{C}-\text{CH}_2\text{F}}}}
+
\underset{\substack{\text{0.0065}\\\text{--}}}{\underset{\text{CH}_3}{\overset{\text{CF}_3}{\text{H}_3\text{C}-\text{C}-\text{CF}_3}}}
\rightarrow
$$

Octafluoroneopentanes

$$
\underset{\substack{\text{0.6545}\\\text{0.5144}}}{\underset{\text{CHF}_2}{\overset{\text{CF}_3}{\text{FH}_2\text{C}-\text{C}-\text{CHF}_2}}}
+
\underset{\substack{\text{0.1636}\\\overline{\text{0.4858}}}}{\underset{\text{CHF}_2}{\overset{\text{CHF}_2}{\text{F}_2\text{HC}-\text{C}-\text{CH}_2\text{F}}}}
+
$$

Heptafluoroneopentanes:

$$
\underset{\substack{\text{0.4091}\\\overline{\text{1.0000}}}}{\underset{\text{CHF}_2}{\overset{\text{CHF}_2}{\text{FH}_2\text{C}-\text{C}-\text{CHF}_2}}}
+
\underset{\substack{\text{0.4091}\\\text{--}}}{\underset{\text{CH}_2\text{F}}{\overset{\text{CF}_3}{\text{FH}_2\text{C}-\text{C}-\text{CHF}_2}}}
+
\underset{\substack{\text{0.1364}\\\text{--}}}{\underset{\text{CHF}_2}{\overset{\text{CF}_3}{\text{H}_3\text{C}-\text{C}-\text{CHF}_2}}}
\longrightarrow
\underset{\substack{\text{0.0455}\\\text{--}}}{\underset{\text{CH}_2\text{F}}{\overset{\text{CF}_3}{\text{H}_3\text{C}-\text{C}-\text{CF}_3}}}
+
$$

Nonafluoroneopentanes:

$$
\underset{\substack{\text{0.1091}\\\text{--}}}{\underset{\text{CH}_2\text{F}}{\overset{\text{CF}_3}{\text{FH}_2\text{C}-\text{C}-\text{CF}_3}}}
+
\underset{\substack{\text{0.0727}\\\text{--}}}{\underset{\text{CHF}_2}{\overset{\text{CF}_3}{\text{H}_3\text{C}-\text{C}-\text{CF}_3}}}
\longrightarrow
\underset{\substack{\text{0.4909}\\\overline{\text{0.7973}}}}{\underset{\text{CHF}_2}{\overset{\text{CF}_3}{\text{F}_2\text{HC}-\text{C}-\text{CHF}_2}}}
+
\underset{\substack{\text{0.4909}\\\text{0.2011}}}{\underset{\text{CHF}_2}{\overset{\text{CF}_3}{\text{FH}_2\text{C}-\text{C}-\text{CF}_3}}}
+
\underset{\substack{\text{0.0182}\\\text{--}}}{\underset{\text{CF}_3}{\overset{\text{CF}_3}{\text{H}_3\text{C}-\text{C}-\text{CF}_3}}}
\rightarrow
$$

Decafluoroneopentanes:

$$
\underset{\substack{\text{0.8182}\\\overline{\text{1.0000}}}}{\underset{\text{CHF}_2}{\overset{\text{CF}_3}{\text{F}_2\text{HC}-\text{C}-\text{CF}_3}}}
+
\underset{\substack{\text{0.1818}\\\text{--}}}{\underset{\text{CHF}_2}{\overset{\text{CF}_3}{\text{FH}_2\text{C}-\text{C}-\text{CF}_3}}}
\longrightarrow
\underset{\substack{\text{1.0000}\\\text{1.0000}}}{\underset{\text{CF}_3}{\overset{\text{CF}_3}{\text{F}_2\text{HC}-\text{C}-\text{CF}_3}}}
$$

Undecafluoroneopentane

$$
\longrightarrow
\underset{\substack{\text{1.0000}\\\text{1.0000}}}{\underset{\text{CF}_3}{\overset{\text{CF}_3}{\text{F}_3\text{C}-\text{C}-\text{CF}_3}}}
$$

F-Neopentane

results are those where two or more isomers are isolated. However single isomer products may be considered at least five fold probably ten fold larger than any non-detected, non-isolated isomers.

The results indicate that substitution is near statistical until one reaches the pentafluoroneopentane. At this point only the most symmetrical isomer is isolated. This would indicate that a hydrogen of a CH_3 group is more reactive than a hydrogen of a CH_2F or CHF_2 group. At the next step only one hexafluoroneopentane is isolated indicating that a hydrogen on a CH_2F is more readily substituted than a CHF_2 however this is also statistically the predicted major isomer. The more definitive case comes at the heptafluoro-neopentane where again the only isomer isolated is the most symmetrical. However here the unsymmetrical $(CF_3)C(CH_2F)_2(CHF_2)$ isomer is of equal probability. This is a more convincing case for the greater reactivity of hydrogens on CH_2F relative to CHF_2. The octafluoroneopentane case also supports this contention. The theoretical distribution of the unsymmetrical $(CF_3)C(CHF_2)_2(CH_2F)$ isomer to the symmetrical $C(CHF_2)_4$ is 4:1 however the experimental distribution is closer to 1:1. Again at the nonafluoroneo-pentane the lowered reactivity of the CHF_2 group is indicated in that the ratio of isomers $(CF_3)_2C(CHF_2)(CH_2F)$ to $(CF_3)C(CHF_2)_3$ theoretically is 1:1 however the experimental ratio is close to 1:4 with the symmetrical isomer predominating.

Although the experimental numbers themselves are of little theoretical value the experimental isomer ratios compared to the theoretical isomer ratios indicate unequivocally that the reactivities of hydrogen atoms to attack by elemental fluorine can be altered and that hydrogens are not always indiscriminately attacked by fluorine in a purely statistical way. The apparent order of hydrogen reactivity is $CH_3 > CH_2F > CHF_2 >> CF_3$. This order not only parallels the order of steric accessibility of the hydrogen atoms

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but also parallels the expected order of electron density on the hydrogens. The latter effect if controlling probably indicates that fluorine prefers the more electron rich hydrogens. This at least suggests that selectivity in a molecule might be achieved by altering the electron density of the carbon bearing the hydrogen.

Photochemical Assisted Fluorinations

The addition of the photochemical reaction stage to the aerosol fluorinator now permits significantly better utilization of elemental fluorine at least in the low degree of fluorination range. The comparison of PF/N-1 (Figure 3) with F/N-1 (Figure 2) demonstrates that almost a 12 fold decrease in fluorine excess is possible while achieving virtually the same product distribution and similar yields. More importantly however the photochemical stage allows the achievement of high degrees of perfluorination although at the expense of some fragmentation. Yields are still quite high for those "expected" for an elemental fluorine reaction and certainly one utilizing photochemical activation in the final stages. The key to molecular integrity is obviously the fact that molecules entering the gradient photochemical cell are already highly fluorinated (Figures 4 and 5) and are therefore more robust and capable of resisting fragmentation under vigorous attack by both molecular and atomic fluorine. It is significant to note that the photochemical cell has not in nearly a year of use become befouled and to the contrary looks almost as good as the day it was initiated. A ultraviolet transmission spectrum of the 0.015" FEP Teflon film shows that its absorbance curve is near zero and flat until it shuts off at 224 nm in the ultraviolet. It is however of utmost importance to keep the polymer wall near 25°C as it begins to loose its structural rigidity about 50°C forming kinks in the smooth coil. A word of caution is in order, since

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atomic fluorine is produced in the photochemical cell excessive temperatures may cause the FEP Teflon to be attacked with disasterous results at the higher fluorine flows.

The higher fluorine flows produce anomolous results in the product distributions of the neopentane photochemical reactions. Unlike the "dark" reactions which give a successively higher degree of fluorination with increasing concentration, the photochemical reaction begins to produce F-Neopentane. The relative proportions of F-neopentane and lower fluorinated species remain near constant as the fluorine concentration is increased. This effect may be due to increasing fragmentation reducing overall yields which do decrease somewhat.

Survival in the photochemical stage may be dependent on previously achieving a particular degree of fluorination for a given residence time in the photochemical reactor for a given fluorine concentration. The threshold level may be related to fluorine radical chain propagation occurring due to concentration effects. Some support for this may be seen in PF/N-6 where lower component survival rises dramatically when the main carrier is increased three fold. Obviously a good deal of optimization of conditions remains to be done before much more can be said about the photochemical system.

The fluorination of 1,4-dioxane dramatizes the effectiveness of the photochemical stage. The crude product collected from the reactor is better than 90% pure F-1,4-dioxane in yields approaching sixty percent. The extremely difficult direct fluorination of cyclohexane to perfluorocyclohexane can be accomplished in yields exceeding thirty percent and a product purity in excess of ninety percent direct from the reactor. The low yields are due to tar formation in stage one which we should be able to eliminate by reducing the fluorine concentration gradient at this stage.

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Absence of Hydrogen Fluoride Solvolysis

The direct fluorination reaction produces a molecule of hydrogen fluoride for every hydrogen substituted. It was of interest to determine whether acid catalysed cleavage would occur in the reactor system to an appreciable extent. The very acid sensitive ketal, 2,2-dimethyl-1,3-dioxolane was chosen for this determination. The results indicate that HF solvolysis of such groupings is not a problem. It was possible to produce fluoro analogs of the 1,3-dioxolane in very good yields with almost no evidence of HF solvolysis. The photochemical perfluorination went uneventfully and actually produced higher overall yields than the 1,4-dioxane. Whether this lack of solvolysis is general will, of course, require reaction of many different compounds and different functionalities.

Summary

The multistaged aerosol fluorination reactor achieves optimum control over the potentially violent direct fluorination reaction. This system meets all of the criteria enumerated earlier which we, by experience, believe contribute to high yield direct fluorination reactions. It additionally has other distinct advantages in that the degree of fluorination may be controlled; it is a flow process; the process does not depend on the physical properties of the reactant to be fluorinated; reactant throughputs may be varied over a considerable range for a given design; fluorine concentration and temperature conditions may be taylored to the reactivity of the reactant; and most importantly the observation of non-statistical substitution effects suggests that this system might permit the elusive achievement of selectivity in direct fluorinations.

TABLE 1

MASS THROUGHPUT FOR HYDROCARBONS IN THE AEROSOL SYSTEM

HELIUM CARRIER flow-rate [cc/min]	MASS OF HYDROCARBON [mg/h]	MASS THROUGHPUT [mmol/h]
NEOPENTANE: (a)		
63.5	38.2	0.53
84.5	60.6	0.84
98	70.8	0.98
100	71.8	1.00
110	94.6	1.31
126	103.4	1.43
174	115.4	1.60
NEOPENTANE: (b)		
43	150	2.0
101	290	4.0
CYCLOHEXANE: (c)		
8	60	0.71
14.5	87.3	1.04
43.5	245.8	2.92
102	523.8	6.22
2,2-DIMETHYL-1,3-DIOXOLANE: (d)		
19	200	1.96
32	410	4.02
64	630	6.18

Hydrocarbon Reservoir Temperature: (a) −78°C, (b) −63°C,
(c) 0°C, (d) 39°C

TABLE 2

REACTION CONDITIONS FOR AEROSOL FLUORINATIONS OF NEOPENTANE IN A TWO-STAGE REACTOR (S)

Ref. No.	hydrocarbon flow [mmoles/h]	h.c. carrier [cc/min]	main carrier [cc/min]	F_2-flow [cc/min] st. 1	st. 2	Σ	F_2 dil. He flow [cc/min]	hc:F_2	stoichiometry stage 1	2	Σ	% F_2 at end of reactors.	reaction time [sec]
F/N-1	1	101	5000	5	-	5	100 + 20	1:12	1	-	1	0.1	3.7
F/N-2	1	101	2500	5	-	5	20 + 20	1:12	1	-	1	0.19	7.3
F/N-3	1	101	2500	10	-	10	20 + 20	1:24	2	-	2	0.38	7.3
F/N-4	1	101	2500	5	5	10	20 + 20	1:24	1	1	2	0.38	7.3
F/N-5	1	101	2500	5	15	20	20 + 20	1:48	1	3	4	0.75	7.2
F/N-6	1	101	2500	20	-	20	20 + 20	1:48	4	-	4	0.75	7.2
F/N-7	1	101	2500	20	20	40	20 + 20	1:96	4	4	8	1.5	7.2

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TABLE 3

REACTION CONDITIONS FOR AEROSOL FLUORINATIONS OF NEOPENTANE IN A FOUR-STAGE REACTOR (T)

Ref. No.	hydrocarbon flow [mmoles/h]	h.c. carrier [cc/min]	main carrier [cc/min]	F_2-flows [cc/min] stage					F_2 dil He flow [cc/min]
				1	2	3	4	Σ	
F/N-8	1	101	2500	20	20	–	–	40	4 x 20
F/N-9	1	101	2500	20	20	20	–	60	3 x 20 + 10
F/N-10	1	101	2500	20	20	20	20	80	4 x 20
F/N-11	1	101	2500	20	20	20	20	80	4 x 20
F/N-12	1	101	2500	20	20	20	20	80	4 x 20

continued below

Ref. No.	hc:F_2	stoichiometry in stage				Σ	% F_2 at end of react. syst.	reaction time [sec]	temperature [°C] modules		
		1	2	3	4				reactor	#1	#2
F/N-8	1:96	4	4	–	–	8	1.5	5.9	-65	-60	-60
F/N-9	1:144	4	4	4	–	12	2.2	5.9	-65	-60	-60
F/N-10	1:192	4	4	4	4	16	2.9	5.8	-65	-60	-60
F/N-11	1:192	4	4	4	4	16	2.9	5.8	-65	-60	-30
F/N-12	1:192	4	4	4	4	16	2.9	5.8	-65	-60	-30

TABLE 4

REACTION CONDITIONS FOR AEROSOL FLUORINATIONS OF NEOPENTANE IN A FOUR-STAGE
REACTOR + COPPER COIL (U)

Ref. No.	hydrocarbon flow [mmoles/h]	h.c. carrier [cc/min]	main carrier [cc/min]	F_2 flows [cc/min] in stage 1.	2	3	4	Σ	F_2 dil. He flow [cc/min]
F/N-13	1	101	2500	20	20	20	20	80	4 x 20
F/N-14	1	101	2500	20	20	20	20	80	4 x 20
F/N-15	1	101	2500	20	20	20	20	80	4 x 20
F/N-16	1	101	1250	20	20	20	20	80	4 x 20
F/N-17	1	101	600	20	20	20	20	80	4 x 10
F/N-18	1	101	600	20	20	40	40	120	4 x 5
F/N-19	1	101	600	20	20	60	60	160	4 x 10
F/N-20	1	101	400	20	20	60	100	200	4 x 5
F/N-21	4	101	400	20	20	60	100	200	4 x 5

Ref. No.	temperature [°C] reactor	modules #1	#2	coil	stoichiometry hc:F_2	in stage 1	2	3	4	Σ	% F_2	reaction time [sec]
F/N-13	-65	-60	-30	RT	1:192	4	4	4	4	16	2.9	16.8
F/N-14	-65	-30	0	+45	1:192	4	4	4	4	16	2.9	16.8
F/N-15	-65	-30	0	+45	1:192	4	4	4	4	16	2.9	16.8
F/N-16	-65	-30	0	+45	1:192	4	4	4	4	16	5.3	30.6
F/N-17	-65	-30	0	+45	1:192	4	4	4	4	16	9.7	56.3
F/N-18	-65	-30	0	+45	1:288	4	4	8	8	24	14.3	55
F/N-19	-65	-30	0	+45	1:384	4	4	12	12	32	17.25	51.3
F/N-20	-65	-30	0	+45	1:480	4	4	12	20	40	27.7	64.1
F/N-21	-65	-30	0	+45	1:120	1	1	3	5	10	27.7	64

TABLE 5

^{19}F NMR DATA OF FLUORINATED NEOPENTANES

Formula	Ref. No.	Structure	CF$_3$ $\emptyset$ [ppm] a)	J [Hz]	CF$_2$H $\emptyset$ [ppm] a)	J [Hz]	CFH$_2$ $\emptyset$ [ppm] a)	J [Hz]	Integration ratios
C_5H_{12}	*	$C(CH_3)_4$							
$C_5H_{11}F$	ND	$(CH_3)_3C\text{-}CFH_2$					222.7	(t) 46	
$C_5H_{10}F_2$	NL	$(CH_3)_2C(CFH_2)_2$					227.8	(t) 50.9	
$C_5H_{10}F_2$	NF'	$(CH_3)_3C\text{-}CF_2H$			$\sim$128 b)	(d) 57.1			
$C_5H_9F_3$	NQ	$(CFH_2)_3C\text{-}CH_3$					234.6	(t) 49.6	
$C_5H_9F_3$	NK'	$(CH_3)_2C(CFH_2)(CF_2H)$			$\sim$131 b)	(d) 53.4	$\sim$228 b)	(t) 45.8	d:t $\approx$ 2:1
$C_5H_8F_4$	NS	$C(CFH_2)_4$					240.1	(t) 45.8	
$C_5H_8F_4$	NN	$(CH_3)_2C(CF_2H)_2$			129.2	(d) 53.4			
$C_5H_8F_4$	NO	$(CFH_2)_2C(CF_2H)(CH_3)$			132.7	(d) 53.4	236.3	(t) 45.8	d:t $\approx$ 1:1
$C_5H_2F_5$	NT	$(CFH_2)_3C\text{-}CF_2H$			131.1	(d) 53.4	241.1	(t) 45.8	d:t $\approx$ 2:3
$C_5H_6F_?$	NR	$(CFH_2)_2C(CF_2H)_2$			130.1	(d) 48.8	242.4	(t) 48.8	d:t $\approx$ 2:1
$C_5H_5F_7$	NP	$(CF_2H)_3C\ CFH_2$			129.1	(d) 53.4	243.8	(t) 45.8	d:t = 6.8:1
$C_5H_4F_8$	NK	$C(CF_2H)_4$			128.4	(d) 53.4			
$C_5H_4F_8$	NI	$(CF_2H)_2C(CF_3)(CFH_2)$	66.8	(s)	129.3	(d) 51	244.4	(t) 41	s:d:t = 3:4:1
$C_5H_3F_9$	NH	$(CF_2H)_3C\text{-}CF_3$	64.5	(s)	127.8	(d) 51			
$C_5H_3F_9$	NG	$(CF_3)_2C((CFH_2)(CF_2H)$	66.57 c)	(q)	130.1 c)	(d) 52.2	240.4 c)	(t) 45.6	s:d x 1:2
$C_5H_2F_{10}$	NE	$(CF_2H)_2C(CF_3)_2$	64.6 c	(p)	127.29	(d) 54.5			
C_5HF_{11}	NC	$(CF_3)_3C\text{-}CF_2H$	65.4 c	(t)	125.7	53			
C_5F_{12}	NB	$C(CF_3)_4$	65.42 c	(s)					

a) Chemical shifts $\emptyset$ [in ppm] are relative to internal CFCl$_3$; since resolution of the spectra was not very high, only the large geminal F-H couplings were observed.

b) Chemical shift values measured from spectra.

c) Data from LTG-products, chemical shifts are measured from spectra. See References 14 and 37.

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TABLE 6

^{1}H NMR SPECTRA OF FLUORINATED NEOPENTANES [a]

Formula	Ref. No.	Structure	CH$_3$ δ [ppm]	CH$_3$ J[b] [Hz]	CH$_2$F δ [ppm]	CH$_2$F J[b] [Hz]	CHF$_2$ δ [ppm]	CHF$_2$ J[b] [Hz]	Integration Ratios
C$_5$H$_{12}$[c]	*	C(CH$_3$)$_4$	0.94						
C$_5$H$_{11}$F	ND	(CH$_3$)$_3$C-CFH$_2$	0.96	(d) 1.7	4.0	(d) 48			
C$_5$H$_{10}$F$_2$	NL	(CH$_3$)$_2$C(CFH$_2$)$_2$	0.96	(t) 1.8	4.2	(d) 47.6			t:d = 3:2
C$_5$H$_{10}$F$_2$	NF'	(CH$_3$)$_3$C-CF$_2$H	0.99	(d) 1			~7[b]		
C$_5$H$_9$F$_3$	NQ	(CFH$_2$)$_3$C-CH$_3$	1.05	(q) 1.7	4.4	(d) 47.1			g:d = 1:2
C$_5$H$_9$F$_3$	NK'	(CH$_3$)$_2$C$_9$CFH$_2$)(CF$_2$H)	1.06	(m) < 1	4.25	(d) 47.1	5.67	(t) 56.6	m:d:t ~ 7:2:1
C$_5$H$_8$F$_4$	NS	C(CH$_2$F)$_4$			4.6	(d) 46.6			
C$_5$H$_8$F$_4$	NN	(CH$_3$)$_2$C(CF$_2$H)$_2$	1.3				~6	(t)	s:t ~ 3:1
C$_5$H$_8$F$_4$	NO	(CFH$_2$)$_2$C(CF$_2$H)(CH$_3$)	1.1		e)	(m)	5.8	(t) 55.7	s:m:t ~ 3:4:1
C$_5$H$_7$F$_5$	NT	(CFH$_2$)$_3$C-CF$_2$H			4.66	(d) 46.6	6.0	(t) 54.7	d:t ~ 6:1
C$_5$H$_6$F$_6$	NR	(CFH$_2$)$_2$C(CF$_2$H)$_2$			4.7	(d) 46.4	6.1	(t) 54.4	d:t = 2:1
C$_5$H$_5$F$_7$	NP	(CF$_2$H)$_3$C-CFH$_2$			4.9	(d) 46.1	6.2	(t) 54.2	
C$_5$H$_4$F$_8$	NK	C(CF$_2$H)$_4$					6.3	(t) 54	
C$_5$H$_4$F$_8$	NI	(CF$_2$H)$_2$C(CF$_3$)(CFH$_2$)			4.95	(d) 46	6.24	(t) 54	
C$_5$H$_3$F$_9$	NH	(CF$_2$H)$_3$C-CF$_3$					6.3	(t) 53	
C$_5$H$_3$F$_9$	NG	(CF$_3$)$_2$C(CFH$_2$)(CF$_2$H)			4.92	(d) 45.6	6.31	(t) 52.2	f)
C$_5$H$_2$F$_{10}$	NE	(CF$_3$)$_2$C(CF$_2$H)$_2$					6.21	(t) 52.2	f)
C$_5$H$_1$F$_{11}$	NC	(CF$_3$)$_3$C-CF$_2$H					6.255	(t) 54.5	f)
C$_5$F$_{12}$	NB	C(CF$_3$)$_4$							

a) Chemical shifts δ [in ppm] are relative to TMS; they were calculated by assuming that the residual proton on CDCl$_3$ occurs at 7.26 on δ-scale.

b) d = doublet, t = triplet, q = quadruplet, m = multiplet (Note: only basic splittings are given).

c) This signal is a very weak triplet, which does not appear in the print out.

d) from: F. A. Bovey, "Nuclear magnetic resonance spectroscopy," 1969.

e) complex multiplet between 4.3 and 4.6 ppm.

f) data from LTG products, see References 14 and 37.

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TABLE 7

IR MASS SPECTRA AND ELEMENTAL ANALYSIS FOR PARTIALLY FLUORINATED NEOPENTANES:

ND = 1-fluoroneopentane $C_5H_{11}F$

IR: 2960 (vs), 2890 (ms), 1480 (m,br), 1410 (w), 1400 (w), 1380 (sh),

1370 (m), 1360 (sh), 1290 (w,br), 1220 (w,br), 1190 (w), 1045 (s),

1025 (m), 1015 (s), 1005 (m), 905 (w)

MS: CI: 89 (1.1) C_5FH_{10} (M-H); 75 (2.8) C_4FH_8 (M-CH$_3$); 71 (100)

C_5H_{11} (M-F); 69 (3.0) C_5H_9; 59 (1.0) C_3FH_4

EI: 75 (38.5) C_4FH_8; 57 (100) C_3FH_2 or C_4H_9; 55 (61.1) C_3F or

C_4H_7; 47 (57.1) C_2FH_4; 41 (81.6) C_3H_5; 39 (47.3) C_3H_3;

33 (25.8) CFH_2; 29 (71.2) C_2H_5; 27 (37.1) C_2H_3.

NL = 1,3-difluoroneopentane $C_5H_{10}F_2$

IR: 2970 (s), 2900 (m), 1480 (m), 1405 (w), 1370 (w); 1055, 1050, 1040,

1030 (vs); 995, 990 (mw), 910 (w)

MS: CI: 89 (38.3) $C_4F_2H_3$; 75 (18.1) C_3F_2H; 69 (100) C_4FH_2 or C_5H_9:

59 (45.6) C_3FH_4

EI: 75 (89.7) C_3F_2H; 73 (10.4) C_4FH_6; 69 (17.7) C_4FH_2 or C_5H_9;

59 (16.0) C_3FH_4; 55 (76.1) C_4H_7 or C_3F; 53 (12.2) C_4H_5;

51 (12.1) CF_2h or C_4H_3; 47 (100) C_2FH_4; 41 (23.5) C_3H_5;

39 (36.3) C_3H_3; 33 (48.8) CFH_2; 29 (58.1) C_2H_5; 27 (44) C_2H_3.

NF' = 1,1-difluoroneopentane $C_5H_{10}F_2$

IR: 2970 (m), 2880 (w), 1490 (w,br), 1410 (w), 1370 (w),

1290 (w,br), 1110 (s), 1100 (ms), 1085 (ms), 1080 (s),

1030 (mw), 905 (w)

MS: CI: 89 (100) $C_5H_{10}F$ (M-F); 87 (1.8) C_5H_8F; 71 (4.2) C_5H_{11};

69 (11.5) C_4FH_2 or C_5H_9; 59 (5.1) C_3FH_4

EI: 65 (44.6) $C_2F_2H_3$ or C_5H_5; 57 (100) C_3FH_2 or C_4H_9 51 (30.5)

CF_2H or C_4H_3; 47 (18.4) C_2FH_4; 41 (88.3) C_3H_5; 39 (35.1)

C_3H_3; 29 (45.4) C_2H_5; 27 (22.2) C_2H_3

TABLE 7 (CONTINUED)

NQ = Sym. trifluoroneopentane $C_5H_9F_3$

IR: 2970 (m), 2900 (mw), 1470 (w,br), 1390 (w,br), 1290 (w,br), 1200 (w,br), 1050/1040 (vs), 980 (w), 935 (vw)

MS: CI: 117 (40.6) C_5F_3; 87 (100) C_4F_2H or C_5H_8F; 67 (29.9) C_4F or C_5H_7; 59 (64.3) C_3FH_4

EI: 77 (11.6) $C_3F_2H_3$; 59 (20.7) C_3FH_4; 53 (20.4) C_4H_5; 51 (19.3) C_4H_3; 47 (100) C_2FH_4; 43 (12.1) C_2F; 41 (15.1) C_3H_5; 39 (23.5) C_3H_3; 33 (47.8) CFH_2; 29 (19.4) C_2H_5; 27 (26.8) C_2H_3.

Elemental Analysis: Calc. %C 47.62; %H 7.19; %F 45.19

$C_5H_5F_3$ Found: %C 47.68; %H 7.33; %F 45.16; %F

NK' = asym. trifluoroneopentane $C_5H_9F_3$

IR: 2980 (ms); 2900 (w), 1480 (w), 1410 (w), 1370 (w), 1190 (w), 1120 (s), 1110 (ms), 1100 (sh), 1090 (s), 1040 (sh), 1030 (s), 990 (w), 905 (w)

MS: CI: 117 (100) C_5F_3; 87 (66.5) C_4F_2H; 67 (17.5) C_4F

EI: 93 (14.3) C_3F_3; 75 (100) C_3F_2H; 65 (68.5) C_5H_5; 59 (14.5) C_3FH_4; 55 (61.8) C_3F; 51 (30.3) CF_2H; 47 (71.0) C_2FH_4; 43 (10.9) C_2F; 41 (11.4) C_3H_5; 39 (20.1) C_3H_3

Elemental Analysis: Calc. %C 47.62; H 7.19; %F 45.19

$C_5H_9F_3$ Found: %C 47.79; %H 7.41; %F 45.00;

NN = 1,1,3,3-tetrafluoroneopentane $C_5H_8F_4$

IR: 2980 (w,br), 1470 (w,br), 1390 (mw,br), 1240 (mw), 1215 (m), 1180 (m), 1145 (sh), 1130 (ms), 1100 (s), 1080 (sh), 980 (w), 660 (w)

MS: CI: 141 (100) $C_5F_4H_5$

EI: 69 (14.8) C_4FH_2 or C_5H_9; 65 (10.5) C_5H_5; 64 (14.0) C_5H_4; 59 (55.3) C_3FH_4; 57 (12.2) C_3FH_2; 51 (100) CF_2H 39 (15.2) C_3H_3

TABLE 7 (CONTINUED) (b)

NO = asym. tetrafluoroneopentane $C_5H_8F_4$

IR: 2980 (m), 2900 (w), 1470 (w,br), 1410/1390/1370 (w,br),

1280 (w), 1210, 1190 (br), 1090 (s,br), 1030 (s), 975 (w),

930 (w) 900 (vw), 840 (vw), 690 (w), 640 (vw)

MS: CI: 133 (14.8) $C_3F_5H_2$?; 125 (14.7) C_4F_4H; 119 (18.9) $C_5F_3H_2$

117 (100) C_5F_3; 105 (56.1) C_4F_3; 85 (46.0) C_5FH_6; 75 (52.6)

C_3F_2H; 73 (12.8) C_4FH_6

EI: 93 (26.5) C_3F_3; 77 (15.7) $C_3F_2H_3$; 73 (48.6) C_4FH_6; 71 (10.7)

C_4FH_4; 59 (27.2) C_3FH_4; 53 (16.9) C_4H_5; 59 (27.2) C_3FH_4;

53 (16.9) C_4H_5; 51 (61.2) CF_2H; 47 (100) C_2FH_4; 41 (23.4) C_3H_5;

39 (28.1) C_3H_3; 33 (35.8) CFH_2; 29 (10.7) C_2H_5; 27 (17.4) C_2H_3

Elemental Analysis: Calc. %C 41.67; %H 5.60; %F 52.73

$C_5H_8F_4$ Found: %C 39.57; %H 5.51; %F (54.92)

NT = sym.-pentafluoroneopentane

IR: 2986 (s), 2923 (m), 1480 (m), 1388 (br,m), 1282 (m), 1205 (sh),

1198 (ms), 1180 (ms), 1165 (sh), 1108 (ms), 1099 (sh), 1090 (s),

1080 (sh), 1065 (sh), 1057 (m); 1044 (sh), 1037 (vs)

MS: CI: 181 (6.9) C_4F_7 (imp) 163 (4.7) $C_5F_5H_8$; 143 (4.0) $C_5F_4H_7$ 141

(5.6) $C_5F_4H_5$; 125 (16.6) C_4F_4H; 123 (100.0) $C_5F_3H_6$; 105 (78.7)

C_4F_3; 103 (19.0) $C_5F_2H_5$; 85 (15.5) SiF_3; 79 (12.9) $C_3F_2H_5$;

77 (54.8) $C_3F_2H_3$; 73 (15.1) C_4FH_6; 65 (5.3) $C_2F_2H_3$; 59 (30.0)

C_3FH_4

EI: 163 (5.0) C_4F_6H(imp); 131 (5.9) C_3F_5; 119 (6.9) C_2F_5; 111

(29.5) $C_4F_3H_6$; 110 (35.3) $C_4F_3H_5$; 109 (9.6) $C_4F_3H_4$ 95 (20.7)

$C_3F_3H_2$; 92 (14.2) $C_4F_2H_6$; 91(100.0) $C_4F_2H_5$; 89 (12.5) $C_4F_2H_3$;

TABLE 7 (CONTINUED)(c)

85 (11.8) $C_3F_2H_9$; 77 (77.1) $C_4F_2H_5$; 71 (25.3) C_4FH_5; 69 (26.6)

CF_3; 65 (44.1) $C_2F_2H_3$; 59 (55.4) C_3FH_4; 58 (28.7) C_3FH_3; 57

(14.3) C_3FH_2; 51 (47.1) CF_2H; 44 (13.2) C_2FH; 43 (46.6) C_2F

39 (11.2) C_3H_3; 33 (12.3) CFH_2.

Elemental Analysis: Calc. %C 37.05; %H 4.35 %F 58.60

$C_5H_7F_5$ Found: %C 37.40; %H 4.67 %F 58.46

NR = hexafluoroneopentane $C_5H_6F_6$

IR: 2980 (mw), 2910 (w), 1480 (w), 1390 (m), 1290 (w,br), 1190 (s),

1110 (s,br), 1060 (sh), 1040 (sh), 970 (w), 910 (m), 670 (w)

MS: CI: 141 (100) $C_5F_4H_5$; 121 (11.4) $C_5F_3H_4$; 91 (25.0) $C_4F_2H_5$; 77

(49.6) $C_3F_2H_3$; 65 (31.9) C_5H_5; 59 (61.0) C_3FH_4

EI: 95 (45.3) $C_3F_3H_2$; 91 (10.1) $C_4F_2H_5$; 89 (12.2) $C_4F_2H_3$; 77

(80.6) $C_3F_2H_3$; 65 (10.0) C_5H_5; 59 (100) C_3FH_4; 57 (19.2)

C_3FH_2; 51 (75.1) CF_2H; 39 (12.4) C_3H_3; 33 (12.5) CFH_2

Elemental Analysis: Calc. %C 33.35; %H 3.36; %F 63.29

$C_5H_6F_6$ Found: %C 33.25; %H 3.44; %F 62.91

NP = heptafluoroneopentane $C_5H_5F_7$

IR: 3000 (sh), 2975 (w), 2900 (sh), 1480 (w), 1390 (m), 1190 (vs,

with several shoulders), 1110 (s), 1070 (s), 1030 (sh), 945

(w), 790 (w), 600 (w)

MS: CI: 217 (11.6) $C_5F_8H_5$; 159 (4.0) $C_5F_5H_4$; 109 (100.0) $C_4F_3H_4$.

EI: 270 (2.6) $C_5F_{11}H$; 219 (3.6) C_4F_9; 181 (1.7) C_4F_7; 145 (3.5)

$C_4F_5H_2$; 131 (5.1) C_3F_5; 127 (14.9) $C_4F_4H_3$; 109 (37.4) $C_4F_3H_4$;

95 (25.9) $C_3F_3H_2$; 89 (10.0) ? ; 77 (100.0) $C_3F_2H_3$; 69 (17.8)

CF_3; 59 (21.3) C_3FH_4; 58 (34.5) C_3FH_3; 57 (12.2) C_3FH_2; 51

(42.0) CF_2H; 43 (28.8) C_2F.

TABLE 7 (CONTINUED)(d)

Elemental Analysis: Calc.   %C 30.32; %H 2.54; %F 67.14

$C_5H_5F_7$ Found: %C 30.54; %H 2.69; %F 67.15

NK = sym. tetrahydro-$\underline{F}$-neopentane $C_5H_4F_8$

IR: 3000 (w), 1395 (m), 1365 (w), 1215 (ms), 1190 (vs), 1145/

1140 (m), 1120 (ms), 1100 (m), 1060 (m), 690 (m)

MS: CI: 107 (48.8) $C_4F_3H_2$; 127 (89.2) $C_4F_4H_3$; <u>87 (100) C_4F_2H</u>

EI: 75 (18.1) C_3F_2H; 57 (19.5) C_3FH_2; <u>51 (100) CF_2H</u>; 47 (15.7)

C_2FH_4

Elemental Analysis: Calc.   %C 27.79; %H 1.87; %F 70.34

$C_5H_4F_8$ Found: %C 27.83; %H 1.89; %F 69.99

NI = asym. tetrahydryl-$\underline{F}$-neopentane $C_5H_4F_8$

IR: 3000 (w), 1400 (w), 1380 (m), 1305 (m), 1260 (sh), 1240 (vs),

1170 (m), 1120 (s), 1110 (sh), 1060 (s), 1025 (mw), 680 (mw)

MS: CI: <u>145 (100) $C_4F_5H_2$</u>; 125 (11.8) C_4F_4H; 119 (12.1) $C_5F_3H_2$; 117

(11.1) C_5F_3;

EI: 75 (13.4) C_3F_2H; 69 (17.0) CF_3; <u>51 (100) CF_2H</u> 33 (16.6) CFH_2

Elemental Analysis: Calc.   %C 27.79; %H 1.87; %F 70.34

$C_5H_4F_8$ Found: %C 27.90; %H 1.93; %F 70.54

NH = sym. trihydryl-$\underline{F}$-neopentane $C_5H_3F_9$

IR: 3000 (w), 1380 (m), 1275 (s), 1240 (s), 1170 (m), 1100 (m),

1055 (m), 1010 (mw), 980 (w), 690 (mw), 660 (w)

MS: CI: <u>127 (100) $C_4F_4H_3$</u>

EI: 77 (3.6) $C_3F_2H_3$; 69 (12.1) CF_3; 57 (3.1) C_3FH_2; <u>51 (100) CF_2H</u>;

31 (4.7) CF

Elemental Analysis: Calc.   %C 25.66; %H 1.29; %F 73.05

$C_5H_3F_9$ Found: %C 25.90; %H 1.56; %F 72.73

TABLE 7 (CONTINUED)(e)

NG = 2.2-(bistrifluoromethyl)-1.1.3-trifluoropropane

IR: 3013 (w), 2999 (sh), 2930 (vw), 1485 (vw), 1412 (sh), 1400 (m),

1375 (m), 1315 (s), 1300 (sh), 1280 (vs), 1258 (vs), 1202 (mw),

1178 (m), 1126 (m), 1106 (m), 1072 (ms), 1025 (ms), 980 (w),

876 (mw), 845 (vw), 818 (vw), 735 (w), 705 (vw), 678 (vw)

MS: CI: 215 (2.2) $C_5H_3F_8$; 203 (3.4) $C_4H_3F_8$; 193 (13.3) C_5F_7; 145

(36.7) $C_4F_5H_2$; 127 (10.9) $C_4F_4H_3$; 119 (5.4) C_2F_5; 107 (5.0)

$C_4F_3H_2$; 101 (8.5) C_2F_4H; 95 (10.9) $C_3F_3H_2$; 79 (100.0) $C_3F_2H_5$;

77 (24.5) $C_3F_2H_3$

EI: 182 (8.0) C_4F_7H; 181 (6.6) C_4F_7; 164 (9.7) $C_4F_6H_2$; 163 (35.8)

95 (95.7) $C_3F_3H_2$; C_4F_6H; 145 (100.0) $C_4F_5H_2$; 113 (33.8) C_3F_4H; 96 (17.1) $C_3F_3H_3$;

77 (17.2) $C_3F_2H_3$; 75 (13.4) C_3F_2H; 69 (37.3) CF_3; 51 (34.9)

CF_2H

Elemental Analysis: Calc. %C 25.66; %H 1.29; %F 73.05

$C_5H_3F_9$ Found: %C 25.87; %H 1.33; %F 72.65

Intensity symbols used in IR-Listings are:

vs very strong, s strong, ms medium-strong, m medium, sh shoulder,

mw medium-weak, w weak, vw very weak, br broad.

TABLE 8

% PRODUCT DISTRIBUTIONS FROM SELECTED AEROSOL FLUORINATIONS OF NEOPENTANE
(ESTIMATED FROM PEAK AREAS OF GLC-TRACES)

	F/N-1	F/N-6	F/N-7	F/N-11	F/N-16	F/N-17	F/N-20	F/N-21
*	4.0	0.5	0.3	* = unreacted neopentane				
NA						0.3	4.0	4.0
NB						0.6	9.2	9.0
NC						4.4	24.0	19.4
ND	21.8	7.6	3.2					
NE					0.7	11.2	32.6	18.6
NF'	4.3	2.5	1.6					
NG					4.1	5.1	3.3	5.0
NH					3.9	18.9	20.8	14.7
NI					15.7	17.4		10.3
NK'	10.7	10.1	8.7					
NK					12.4	18.7	6.2	10.2
NL	37.9	20.1	10.3					
NM				4.6	9.6	3.5		1.5
NN				1.6	1.5			
NO	6.5	17.4	23.9	14.7	7.4			
NF		2.8	3.8	14.3	6.4			
NP		0.9	1.3	6.1	18.1	15.2		6.5
NQ	12.8	16.2	14.0	2.2				
NR		4.1	7.6	24.7	14.9	3.5		0.7
NS	1.8	(3.6)	(5.1)					
		17.8	25.3					
NT		(14.2)	(20.2)	31.8	5.3	1.3		

TABLE 9

IDENTITIES OF PRODUCTS FROM NEOPENTANE FLUORINATIONS

Ref. No.	Structure	Name
NA	$F-C(CF_3)_3$	perfluoroisobutane
NB	$C(CF_3)_4$	perfluoroneopentane[14,32]
NC	$CF_2H-C(CF_3)_3$	undecafluoroneopentane[32]
		$\equiv$ 1-hydryl-$\underline{F}$-neopentane
ND	$CFH_2-C(CH_3)_3$	1-fluoroneopentane
NE	$(CF_2H)_2C(CF_3)_3$	sym. decafluoroneopentane[32]
		$\equiv$ 1,3-dihydryl-$\underline{F}$-neopentane
NF'	$CF_2H-C(CH_3)_3$	1,1-difluoroneopentane
NG	$CFH_2-C(CF_2H)(CF_3)_2$	asym. nonafluoroneopentane
		$\equiv$ 1,1,3-trihydryl-$\underline{F}$-neopentane
NH	$CF_3-C(CF_2H)_3$	sym. nonafluoroneopentane
		$\equiv$ 1,1,1,3,3-pentafluoro-2,2-bis(difluoromethyl)propane
NI	$CF_3-C(CFH_2)(CF_2H)_2$	asym. octafluoroneopentane
		$\equiv$ 1,1,1,3-tetrafluoro-2,2-bis(difluoromethyl)-propane
NK	$C(CF_2H)_4$	sym. octafluoroneopentane
		$\equiv$ 1,1,3,3-tetrafluoro-2,2-bis(difluoromethyl)-propane
NK'	$CF_2H-C(CFH_2)(CH_3)_2$	asym. or 1,1,3-trifluoroneopentane
NL	$(CH_3)_2C(CFH_2)_2$	sym. or 1,3-difluoroneopentane
NN	$(CF_2H)_2C(CH_3)_2$	1,1,3,3-tetrafluoroneopentane
NO	$CF_2H-C(CH_3)(CFH_2)_2$	asym. tetrafluoroneopentane
		$\equiv$ 1,1-difluoro-2,2-bis(fluoromethyl)propane
NP	$(CF_2H)_3C-CFH_2$	heptafluoroneopentane
		$\equiv$ 1,1,3-trifluoro-2,2-bis(difluoromethyl)propane
NQ	$(CFH_2)_3C-CH_3$	sym. trifluoroneopentane
		$\equiv$ 1-fluoro-2,2-bis(fluoromethyl(propane)
NR	$(CFH_2)_2C(CF_2H)_2$	hexafluoroneopentane
		$\equiv$ 1,1,3,3-tetrafluoro-2,2-bis(fluoromethyl)propane
NS	$C(CFH_2)_4$	sym. tetrafluoroneopentane
		$\equiv$ 1,3-difluoro-2,2-bis(fluoromethyl)propane
NT	$CF_2H-C(CFH_2)_3$	pentafluoroneopentane
		$\equiv$ 1,1,3-trifluoro-2,2-bis(fluoromethyl)propane
*	$C(CH_3)_4$	unreacted neopentane

TABLE 10

REACTION CONDITIONS FOR PHOTOCHEMICAL FLUORINATIONS OF NEOPENTANE IN THE AEROSOL REACTOR DESIGNATED (X)

Ref. No.	hydrocarbon flow [mmoles/h]	h.c. carrier [cc/min]	main carrier [cc/min]	F_2 flows [cc/min] in stage 1	2	3	4	Σ	F_2 dil. He flow [cc/min]
PF/N-1	2	43	400	0.8	0.3	0	0	1.1	4 x 5
PF/N-2	2	43	400	2.0	0	0	0	2.0	4 x 5
PF/N-4	2	43	400	5.0	5.0	0	0	10.0	4 x 5
PF/N-5	2	43	400	10.0	0	0	0	10.0	4 x 5
PF/N-6	4	100	1200	20.0	20.0	0	0	40.0	4 x 5
PF/N-7	1	101	400	20.0	20.0	60.0	100.0	200.0	4 x 5

Ref. No.	temperature [°C] reactor	modules #1	#2	coil	hc:F_2	stoichiometry in stage 1	2	3	4	Σ	% F_2	reaction time [sec]
PF/N-1	-65	-30	0	RT	1:1.3	0.08	0.03	0	0	0.11	0.24	175
PF/N-2	-65	-30	0	RT	1:2.4	0.20	0	0	0	0.20	0.43	175
PF/N-3	-65	-30	0	RT	1:6.0	0.50	0	0	0	0.50	1.07	174
PF/N-4	-65	-30	0	RT	1:12.0	0.50	0.50	0	0	1.00	2.11	172
PF/N-5	-65	-30	0	RT	1:12.0	1.00	0	0	0	1.00	2.11	172
PF/N-6	-65	-30	0	RT	1:24.0	1.00	1.00	0	0	2.00	2.94	60
PF/N-7	-65	-30	0	RT	1:48.0	4.0	4.0	12.0	20.0	40.0	27.74	113

TABLE 11

REACTION CONDITIONS FOR PHOTOCHEMICAL FLUORINATIONS OF 1,4-DIOXANE (PF/D); CYCLOHEXANE (PF/C) AND 2-2-DIMETHYL-1,3-DIOXOLANE (PF/DMD) IN THE AEROSOL REACTOR DESIGNATED (X)

Ref. No.	hydrocarbon flow [mmoles/h]	h.c. carrier [cc/min]	main carrier [cc/min]	F$_2$ flows [cc/min] in stage 1	2	3	4	Σ	F$_2$ dil. He flow [cc/min]
F/D-1**	1	63.5[a]	400	20	20	60	100	200	4 x 5
PF/D-1	2	63[b]	400	20	20	60	100	200	4 x 5
PF/C-1	2	29[a]	400	20	20	60	100	200	4 x 5
PF/DMD-1	2	20[c]	400	20	20	60	100	200	4 x 5

*Hydrocarbon reservoir temp: (a) 0°C (b) 10°C (c) 39°C

Ref. No.	temperature [°C] reactor	modules #1	#2	coil	hc:F$_2$	stoichiometry in stage 1	2	3	4	Σ	% F$_2$	reaction time [sec]
F/D-1**	-65	-30	0	RT/45°C**	1:480	6	6	18	30	60	29.3	134
PF/D-1	-65	-30	0	RT	1:240	3	3	9	15	30	29.3	119
PF/C-1	-65	-30	0	RT	1:240	2	2	6	10	20	30.8	125
PF/DMD-1	-65	-30	0	RT	1:240	2.4	2.4	7.2	12	24	31.2	127

**Reactor designation (V) two coils no UV.

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